

94-1 Research and Development Project
Lead Laboratory Support

Status Report
January 1–March 31, 1997

Los Alamos
NATIONAL LABORATORY

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*Compiled by
Nora A. Rink*

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94-1 RESEARCH AND DEVELOPMENT PROJECT LEAD LABORATORY SUPPORT

**Status Report
January 1–March 31, 1997**

**Compiled by
Nora Rink**

ABSTRACT

This status report is published for Los Alamos National Laboratory 94-1 Research and Development Project Support. The Department of Energy Office of Environmental Management funds these projects in order to support the storage or disposal of legacy plutonium and plutonium-bearing materials that resulted from weapons production throughout the DOE complex. This report summarizes status and technical progress for Los Alamos 94-1 R&D projects during the second quarter of fiscal year 1997.

INTRODUCTION

This is the sixth status report published for Los Alamos 94-1 Research and Development Project Lead Laboratory Support. The projects are funded by the Department of Energy Office of Environmental Management to provide support for storage or disposal of legacy plutonium and plutonium-bearing materials resulting from weapons production throughout the DOE complex. Descriptions and milestones for fiscal year 1997 Los Alamos 94-1 Research and Development projects are found in report LA-18261-PR, "94-1 Research and Development Project Lead Laboratory Support Technical Program Plan." Figure 1 presents the work breakdown structure for this effort. The present document reports status and technical progress for funded Los Alamos 94-1 R&D projects.

Reports for three projects—Actinide-Organic Interactions, Plutonium Diffusion Science, and Mineral Waste Forms—are not available for this quarter.

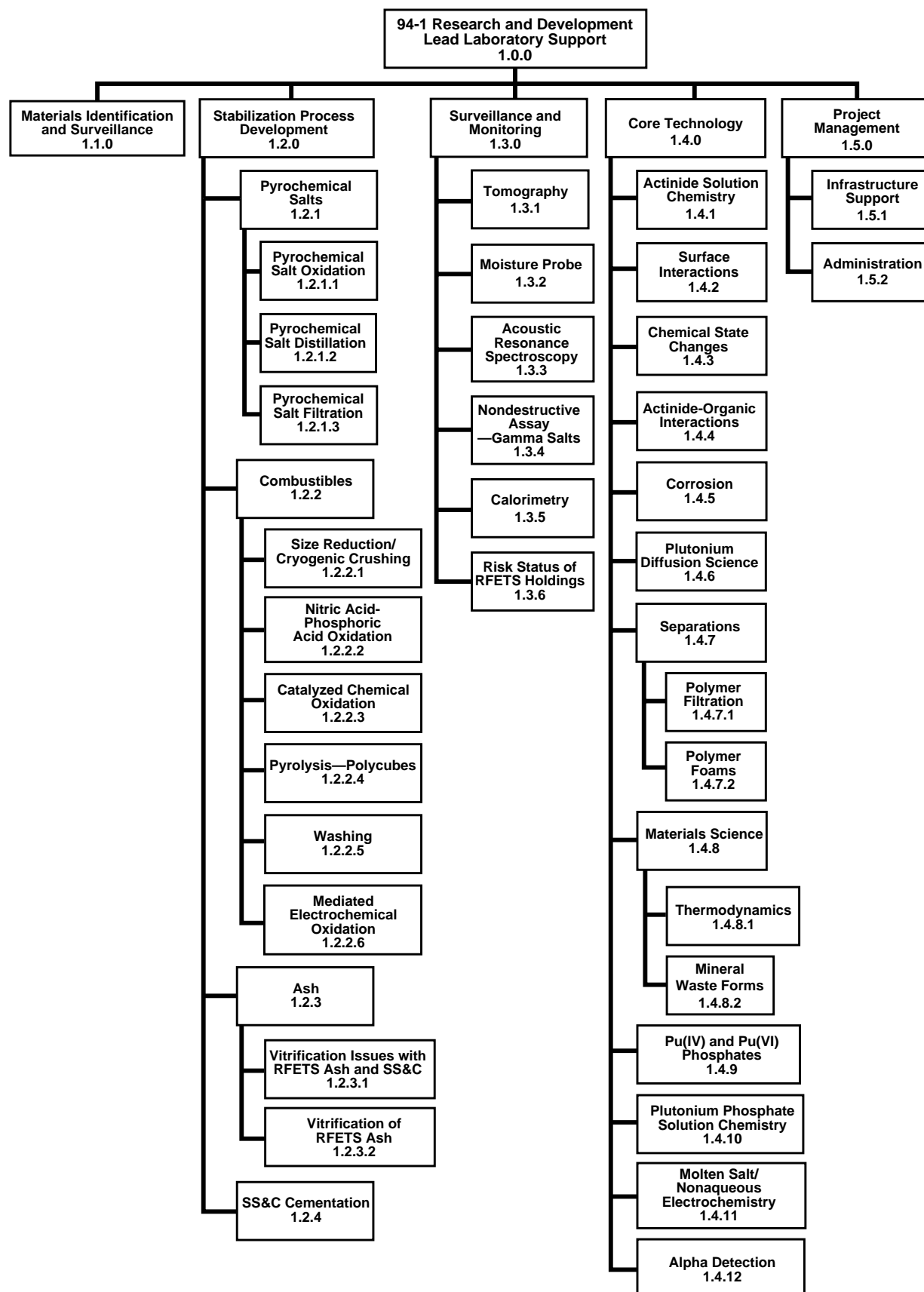


Fig. 1. Work breakdown structure.

Surveillance:**Materials Identification and Surveillance**

Principal Investigators: David R. Horrell
Richard E. Mason

Task Description. The objective of the Materials Identification and Surveillance (MIS) project is to identify materials to be stored in Department of Energy standard 3013-96 (DOE-STD-3013-96)¹ containers and the processing necessary for stabilization of these materials. Representative plutonium oxide materials destined for DOE-STD-3013-96 storage are being shipped to Los Alamos National Laboratory where they will be characterized and their storage behavior determined. The MIS working group that oversees this work is composed of individuals from Rocky Flats Environmental Technology Site (RFETS), Babcock and Wilcox Hanford Company (BWHC), Savannah River Site (SRS), and Los Alamos. At Los Alamos, MIS project researchers develop methods to increase the accuracy and efficiency of characterizing a variety of materials, models thermal profiles of materials in storage configuration, conducts experimentation on thermal profiles to support the modeling, and tests containers for RFETS.

Status/Accomplishments.

Item Evaluations. We have received 9 items from BWHC and are expecting 24 items from RFETS and approximately 10 items from SRS. These items represent materials to be

canned in DOE-STD-3013-96 containers at the several sites. The 9 BWHC items are packaged in produce cans. Two of those items are currently being processed. Processing includes photography and videotaping, real-time radiography, gas analysis of the sealed containers, thermal desorption/mass spectroscopy, thermogravimetric analysis, elemental analysis, particle size/surface area, loss-on-ignition (LOI), bulk and tap density measurements, supercritical fluid extraction for water, and long-term surveillance storage. Los Alamos researchers developed and successfully demonstrated the gas sampling fixture and method for use on sealed storage containers. We are conducting accelerated aging tests on the materials at elevated temperatures that result in determination of evolved gaseous constituents.

The first shipment of approximately half of the RFETS items is expected to arrive in April. SRS materials are expected to arrive in August.

Initial Experimentation. The report on the impure oxide ATL27960 has been completed.² The report on the mixed oxide PUUOXBC05 is in final draft.³ Results of experiments that demonstrate the gas-sampling system using the possibly pressurized Argonne can HRA-90-5-191 from the

Los Alamos Plutonium Facility (TA-55) vault are also available.⁴

The mixed plutonium-uranium oxide PUUOXBC05 was produced and sealed in a food-pack container in November 1983. After 18 years in storage, this material was analyzed using the 3013-96 storage criteria. The inner can, slightly corroded on the bottom seal, was enclosed in a plastic bag. The loss-on-ignition after calcination at 950°C for 2 h is 0.4 mass %, meeting 3013-96 criteria. As received, the plutonium analysis indicated 44 mass %; uranium concentration 18 mass %. After calcination, the concentration of plutonium was 49 mass %. The maximum mass increase caused by the oxidation of UO_3 is 0.72 g/100 g.

Sample Analysis PPSL-365. PPSL-365, the first item from the BWHC vertical calciner, has been evaluated and loaded into long-term storage containers. There are no preliminary indications of a change in pressure in the surveillance containers. We have not yet done an initial gas analysis on these containers. The container was packaged in July 1996, and it was opened in February 1997. Of specific interest are the gas analyses that indicate the loss of oxygen and the initial formation of hydrogen and carbon dioxide (CO_2). The density of this material was found to be about 2.2 g/cc. SCCO_2 extraction indicates no water was present when the item was received. The vertical calciner processing heats the materials to 1000°C and no water was expected; however, LOI evaluation at BWHC and upon receipt at Los Alamos both indicated 0.4 mass % before further

calcination took place at Los Alamos. An LA series report on all material characterization is being prepared.

Sample Analysis ARF-102-85-295.

The second BWHC item, ARF-102-85-295, has been placed in the glovebox. The outer produce can has been sampled. No data are yet available.

Analytical Development.

Supercritical Fluid CO_2 Qualification for Water Measurement. The fact that residual water remains after calcination is the major concern for pressurization potential in a DOE-STD-3013-96 storage container. The DOE standard 3013-96¹ requires a <0.5 mass % LOI for stored materials. Of concern in the use of the LOI method to detect the presence of hydrogenous materials is the fact that weight loss from heating may have several components, only one of which is water. An analytical method using supercritical fluid CO_2 (SCCO_2) to extract all water from pure plutonium oxides, including water that is chemically bound, is under development. SCCO_2 has several attractive features.

- SCCO_2 is very effective at solubilizing highly polar molecular species, such as water and organic compounds.
- SCCO_2 does not readily dissolve nonpolar, inorganic compounds, such as chlorides, oxides, and phosphates.
- Because of the low temperatures involved, typically 35°C–100°C, the extraction process does not result in the decomposition of the

extracted species, as is the case during LOI measurement; i.e., the impurity, whether it is water or some organic compound, can be recovered intact for subsequent analysis.

- This impurity analysis can easily be incorporated into the SCCO₂ experimental arrangement, so that a real-time analytical method is possible.

Preliminary results have been successful. The results of the experimentation will be presented for complex-wide peer review in June. All indications point to successful implementation of this process as an analytical tool by the end of fiscal year 1997. We are also evaluating equipment, for use with packaging systems, to produce efficient and cost-effective analysis.

X-Ray Fluorescence. We are evaluating x-ray fluorescence technology for determination of the elemental constituents in materials to be placed in DOE-STD-3013-96 containers. We believe the technique will give satisfactory answers in less time and with less cost per sample than does inductively coupled plasma elemental analysis that has been used to date. Also, Materials Disposition (MD) personnel are finding that they must identify the impurities in the materials destined for immobilization. The MD organization is particularly interested in assessing the capability of using x-ray fluorescence for fast and

inexpensive elemental analysis in line with a packaging system such as that being installed at RFETS.

Other Developments. Acoustic resonance spectroscopy for identifying gas species in containers and moisture probe to measure water within a container are reported under those headings elsewhere in this quarterly report. Laser-induced breakdown spectroscopy to look for evolution of gases in the container and Raman spectroscopy experimentation for determination of water on oxides are being delayed by other facilities priorities.

Thermal Modeling and Temperature Measurements of BNFL Containers.

Metal Storage. For metal storage measurements, we designed the gas and thermocouple passthrough modifications for the British Nuclear Fuels Limited (BNFL) consolidated procurement storage vessels. These modifications are intended to minimize heat loss through a thermocouple well. The importance of maintaining the heat conductance path through the bottom and walls of the BNFL storage vessels prompted this design. This experimental setup will make it possible to obtain accurate data that is important for validating the thermal model. Also, the design allows two temperature measurements on the outside wall of each container and of the stored plutonium material. These modifications are depicted in Fig. 2.



Fig. 2. Modified BNFL-type container for use in measuring temperatures in mock-up storage packages.

Various gases will be exchanged within the two hermetically sealed cans through the two 1/4-in. tubes that will be sealed by Nupro™ bellows valves.

Thermocouples will be cemented to the plutonium metal and on the outside of all containers. Omegabond 200™ is a high-temperature, highly thermally conductive cement that will be used to bond the thermocouples. The larger 5/8-in. tubes that are

welded to the lids are the thermocouple passthroughs.

All of these modifications are finished. The thermocouples, valves, and MKS™ pressure transducers have been delivered by the respective manufacturers.

We will process a pit to obtain a plutonium metal button. This button will be placed in a Vollrath can and then in the previously mentioned

BNFL cans. Los Alamos Nuclear Materials Technology Division Measurement/Accountability Group packaging section personnel will weld the cans in their helium glovebox.

Alpha Beta Phase Transformation

Experiment. The Los Alamos Nuclear Materials Technology Division Advanced Technology Group has agreed to lend us their pit-burst-test equipment so that strain measurements can be made while the alpha plutonium ingot expands in the primary container during temperature cycling. This equipment has video capabilities.

We fabricated and welded a 6.5-in. Conflat™ flange on a storage container. This is necessary in order to test the strain gauges by measuring small deflections of the vessel while pressurizing with air. This test must be done before placing the container with attached strain gauges into the glovebox.

We submitted a request to Nuclear Materials Technology Division Weapon Component Technology Group foundry supervisor for his personnel to cast an alpha plutonium ingot that will be 0.020-in. smaller in diameter than the inner diameter of the storage container. This casting should be completed in May 1997.

References

1. "Criteria for Preparing and Packaging Plutonium Metals and Oxides for Long-Term Storage," DOE-STD-3031-96 (U.S. Department of Energy, Washington, DC, 1996).
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***Stabilization Process Development:
Pyrochemical Salts—Pyrochemical Salt Oxidation***

Principal Investigator: James A. McNeese

Task Description. The task of Los Alamos National Laboratory researchers is to demonstrate treatment methods for oxidizing wet or reactive pyrochemical salts. The objective is to develop and transfer to Rocky Flats Environmental Technology Site (RFETS) process technology that will stabilize reactive metals contained in these pyrochemical salts. This stabilization process is intended to prevent dangerous levels of hydrogen gas generation during storage and to minimize corrosion from water interactions with the salts and with their containers or drums. We are focusing on optimization of the oxidation process that prepares feed for the salt distillation process. This process requires oxidized salts as feed for optimum performance. Parametric studies are performed to minimize the amount of chemical oxidant needed to ensure that the oxide heel from the distillation process has the maximum special nuclear material (SNM) concentration and that the distilled salt has the minimum amount of actinide.

Crucibles from pyrochemical processes exhibit the same reactive characteristics that salt residues contain. A developmental effort continues on stabilization of crucibles.

A further objective is to determine the effectiveness of liquation of the pyrochemical salts after oxidation. Our purpose is to determine the feasibility of using a settling technique as a method of decreasing the amount of salt feed requiring distillation.

Status and Accomplishments.

We are evaluating the performance of oxidized electrorefining salts in the salt distillation process. This evaluation is necessary to ensure that the feed (oxidized salts) for the process is acceptable in the still and to minimize any adverse effects that the oxidized salts will have on the distillation process. We have found that excess carbonate in an oxidized salt will cause foaming in the distillation equipment, causing difficulty in the distillation operation. When oxidation is coupled with distillation of the sodium chloride/potassium chloride salt matrix, the amount of carbonate used to oxidize the salts is critical. Earlier tests on the small-scale distillation equipment did not exhibit the foaming phenomena that we are now seeing in the full-scale distillation equipment. Foaming could be caused by the different design of the larger unit and/or by the higher vacuum levels and the increased distillation rates that we have achieved.

We investigated methods of killing the excess carbonate by the addition of high-surface-area titanium metal sponge and magnesium chloride to decompose the carbonate. These efforts removed most of the carbonate but were not as successful as we had hoped. Also, there were concerns at RFETS that an additional step in the oxidation process was not acceptable. We have found no suitable method for the complete destruction of the excess carbonate. We have, therefore, redirected our efforts to changing the oxidant to a substance that will not cause foaming if an excess amount is fed to the process. Molybdic anhydride (MoO_3) and vanadium pentoxide (V_2O_5) were selected as oxidants based on their melting points and potential to completely oxidize plutonium species. Initial tests on oxidation of plutonium compounds have demonstrated that these compounds do oxidize plutonium and that the resulting material behaves favorably in the salt distillation process.

Based on the recent success with the vanadium and molybdenum compounds, we are concentrating on these reagents as the oxidants

for the pyro-oxidation process. Determination of reagent dose requirements for pyrochemical salts has begun. The stabilized salts from the oxidation process will be closely coupled to the distillation process development effort. Success will be indicated by our ability to minimize reagent needs for complete oxidation, by the absence of foaming in the distillation equipment, and by maximum SNM concentration in the oxide product.

Indications from RFETS show that the oxidation/distillation effort will take precedence over all other tasks for this project. Therefore, the crucible oxidation milestones scheduled for this task will be delayed for several months.

The liquation experiments for this project are scheduled to begin shortly. This effort was hampered by a lack of success in bringing a contract scientist on board for this purpose. A person has been identified at Los Alamos to perform the experiments for this task. Efforts will be made to meet as many milestones as possible in a compressed time frame without compromising the effort on oxidation/distillation.

***Stabilization Process Development:
Pyrochemical Salts—Pyrochemical Salt Distillation***

Principal Investigator: Eduardo Garcia

Task Description. Los Alamos National Laboratory researchers will demonstrate salt distillation equipment. The salt distillation process is designed to separate plutonium pyrochemical salts into a very lean fraction (<100 ppm plutonium) and plutonium oxide suitable for storage under DOE standard 3013-96. The chloride content of the pyrochemical residues are thereby converted into stable, slightly contaminated salt, and the plutonium content is separated into a homogeneous, well-characterized, oxide material suitable for long-term storage.

An alternate process that uses an aqueous dissolution and filtration separation will be investigated for calcium chloride salts.

Status/Accomplishments. To date, 35 runs have been made with the full-scale prototype distillation unit in a plutonium glovebox. Several of these included electrefining residue (ER) salts, previously oxidized by sodium carbonate, as feed material. Some ER residues produced vacuum levels in the distillation unit that were much worse than observed in nonradioactive tests. These salts were also found to have foamed over the feed crucible walls and to have solidified on the base of the evaporation chamber, making it more difficult to open the

unit after the reaction. These effects were ascribed to the large amounts of plutonium in the ER residues, resulting in large absolute amounts of excess sodium carbonate. The equilibrium vapor pressure of carbon dioxide above sodium carbonate at the distillation temperature is about 1 torr. We are therefore rapidly decomposing the excess sodium carbonate to give high background gas pressures and also to cause foaming of the salt. Despite these problems, the distilled salt had a plutonium concentration of below 1 g/kg.

To solve the problems, we are investigating other oxidants as a substitute for sodium carbonate. Several salts oxidized with vanadium pentoxide (V_2O_5) were used as feed material for salt distillation. We obtained these salts from separate experiments in which the V_2O_5 was used to oxidize plutonium metal, plutonium oxychloride, a mixture of metal and oxychloride, and an ERsalt. The vacuum levels observed using these feed materials were back into the 10^{-3} -torr range, no foaming was observed in any run, and in general all these runs had very good results. No salt was left in any distillation heel, and the plutonium concentration levels of the distillate salts were comparable to those in which sodium carbonate was used as

the oxidant. Plutonium concentrations in the distillation heels were all above 50 wt %. Also, one distillation run was performed on a salt that contained plutonium oxychloride and plutonium metal oxidized with molybdenum trioxide (MoO_3). The results of this run were comparable to those using V_2O_5 . In the third quarter of fiscal year 1997, we will focus our effort on molten salt extraction (MSE) residues.

Mechanical stirring has now been introduced for aqueous dissolution of oxidized direct oxide reduction (DOR) calcium chloride salts. Two runs were made with the stirrer; and, in these, the time required for dissolution of the salt was greatly reduced. In one case,

6 kg of salt were dissolved in 8 h, the second 6-kg batch required 15 h for dissolution. These batches were dissolved by water with no hydrochloric acid (HCl) addition; and the filter cakes were found to contain only ~ 10% plutonium. The remainder is most likely undissolved sodium carbonate from the oxidation process and undissolved calcium oxide from the DOR process. Experiments are under way to treat the filter cake with HCl that will generate, from the carbonate and oxide, sodium and calcium chloride salts, which can be dissolved away to further concentrate the plutonium.

***Stabilization Process Development:
Pyrochemical Salts—Pyrochemical Salt Filtration***

Principal Investigator: Bartley B. Ebbinghaus (Lawrence Livermore National Laboratory)

Task Description. The task is to test molten salt filtration as a means to separate and stabilize actinides from spent pyrochemical salts. The process uses a porous ceramic crucible (e.g., zirconia or alumina between 70% and 82% dense) as the filtration medium and is easily adaptable to existing processing equipment and equipment planned for Rocky Flats Environmental Technology Site (RFETS). To perform these tests, Lawrence Livermore National Laboratory (LLNL) personnel are using LLNL's standard pyrochemical furnaces in argon-atmosphere gloveboxes and LLNL's own limited supply of spent salts, primarily calcium chloride (CaCl_2) electror refining salts that are approximately 2–5 years old. These salts are similar in composition to direct oxide reduction (DOR) salts in that they are composed primarily of CaCl_2 . Unlike DOR salts, however, the LLNL salt residues generally contain 10 wt %–20 wt % actinide; some plutonium trichloride (PuCl_3), which is soluble in molten CaCl_2 ; and, in some cases, significant quantities of magnesium oxide (MgO) crucible.

Status/Accomplishments. In the report for the first quarter of fiscal year 1997 (FY97), we stated that the molten salt filtration process appears to be effective for salts with lower contents of actinides and inert

materials. Because DOR salt residues generally contain 2% actinide or less, the process appears to be suitable for these salt residues. It was also concluded in earlier work that a crucible with larger pore size was needed in order to increase the filtration rate.

Since the FY97 first quarterly report, one additional experiment was performed with the existing porous zirconia filtration crucibles. This experiment further verified the earlier conclusions. (See Table 1) In this experiment (run #5), we added 730.6 g of CaCl_2 salt that was essentially void of actinide content to the 362.3 g salt residue from the previous experiment (run #4). The salt was heated to 890°C for 12 h; and 76% of the added salt passed through the filter and 51% of the total salt passed through the filtration crucible. Analytical data on the filtered salt products of two of the previous runs were obtained. In run #1, the filtered product was determined to contain 0.22 wt % plutonium and 0.05 wt % americium. In run #3, the filtered product was determined to contain 0.009% plutonium and 0.0004% americium. These results correspond to actinide removal efficiencies of 96.8% and 99.96%, respectively. The poorer actinide removal efficiency in the first run was probably because of residual

PuCl_3 , which is soluble in CaCl_2 and therefore is able to penetrate the filtration crucible. The filtered product had a slight purple color, indicating the presence of PuCl_3 . The data for all the runs to date are summarized in Table 1.

Most of the effort in the past few months has been geared toward a more carefully designed set of experiments. The preliminary filtration crucibles had small pore

sizes about 1 μm . New alumina crucibles with larger pore sizes of 3 mm, 40 mm, and 100 μm were ordered and have now been received. The plans for the next set of experiments will be to prepare some actual DOR salt residues. Portions from each residue will be tested in crucibles for each pore size to determine the approximate pore size that would allow both a reasonable filtration rate and a satisfactory actinide removal efficiency.

Table 1. Summary of Salt Filtration Tests

Run #	Input Feed Weight	Initial Actinide Content	Primary Heating			Secondary Heating		
			Filtration Time	Filtration Temperature	Percent Salt Removed	Filtration Time	Filtration Temperature	Percent Salt Removed
1	900 g	8 wt %	2 and 2 h	840° and 920°C	69 wt %	4 h	1000°C	1 wt %
2	635 g	24 wt %	4 h	1000°C	0 wt %			
3	712 g	26 wt %	5 h	1000°C	9 wt %	6 h	1060°C	10 wt %
4	603.1 g	0.2 wt %	3 and 4 h	1006° and 807°C	28 wt %	8 h	902°C	12 wt %
5	730.6 g	0 wt %	12 h	890°C	76 wt %			

Stabilization Process Development:
Combustibles—Size Reduction/Cryogenic Crushing

Principal Investigator: Timothy O. Nelson

Task Description. The goal of this project is to demonstrate size reduction technologies for combustibles. Cryogenic grinding is a process of size-reducing materials at low temperature.

Status/Accomplishments.

Franklin Miller™ Shredder. We have developed a special feed attachment to grind the HYTREX™ flow-through filters used in the Los Alamos National Laboratory Plutonium Facility (TA-55). These filters are the spun polypropylene type. This feed shoot allows the filters to be slowly nibbled away. We shredded HYTREX filters at room temperature.

We also have ground Rocky Flats Technology Site (RFETS) flow-through filters for the Washing project. The RFETS filters are the string-wound polypropylene type with a plastic mandrel on the inside. These filters presented a problem in that we were not able to nibble away at the strings. We ended up cutting the strings off the plastic and slowly feeding them into the Franklin Miller shredder. We ran the strings through the shredder two times at room temperature, cooled the plastic mandrels in liquid nitrogen (LN₂), and then ran them through the shredder.

We have also developed a feed attachment for shredding plastic

bottles. This attachment holds the bottles in a vertical position during shredding. The geometry of the cutters is such that the bottles will roll on top of the cutters if the bottles are not held vertically.

The Los Alamos Computing, Information, and Communications Division Photo-Video Group videotaped the filter shredder in the mockup glovebox at the TA-55 training center. We also ran soft wastes, such as plastic bottles and rubber gloves, through the Franklin Miller shredder; and we crushed plastic bottles in the cryocompactor. A story line will be dubbed onto the video.

HEPA Filter Remediation. The high-efficiency particulate air (HEPA) filter remediation project is coming closer to completion.

We performed an endurance test of the 8-in. Delta™ jointer using both plywood and particle board. We cut a 4-ft × 8-ft sheet of 3/4-in. plywood into 6-in.-wide strips and ran the strips through the jointer, removing 1/8 in. of wood from both sides of the plywood. Before and after this operation, pictures were taken of the jointer blades. The plywood didn't dull the blades a noticeable amount, but the particle board did dull the blades. Apparently, particle board is

made of trees and tree roots that sometimes have rocks in them, and these rocks are crushed up in the particle sheets also. The dull blades were reground and are cutting satisfactorily now. The endurance test showed a volume increase of 3.6 times for plywood and 2.8 times for particle board. The particle board makes finer chips than the plywood.

The jointer was modified to make removing 1/8 in. of wood from the filter safer, faster, and easier. Rails were attached to the jointer for a carriage to roll on. The filter is held inside the carriage by two air cylinders, and the carriage is moved across the blades by an electric linear actuator. The unit has been demonstrated on many HEPA filters. An air hammer has been modified to act as a punch to set each of the 24 nails, in the HEPA filters, below the level of the material being cut off.

This system was demonstrated to RFETS personnel in February 1997. During our meeting, it was agreed that we would have a computer control the operation of the jointer, air cylinders, and linear actuator of the HEPA filter shaver. Also it was agreed that we would need a 480-V, 3-phase motor and a dust collection system.

Work on the HEPA filter jointer has continued since the technical review. The system has been wired to be automatically controlled and is now operated by a computer running LabVIEW® software. The only manual operation performed on the filter jointer is the rotating of the filter to cut a new side. A dust collection system has also been developed that uses a special sack to collect the chips. The sack is mounted in a clear tubing container so that the level of chips can be visually monitored. A large 2 1/2-in.-diam see-through hose connects the chip output of the jointer to the sack housing and then to an industrial vacuum blower with a commercial vacuum-cleaner bag that collects the fine dust particles. One HEPA filter produces about 1.5 L of chips. The filter carriage has also been redesigned for a better HEPA filter fit. A blade change-out procedure has also been developed to eliminate the possibility of the glove being cut by the jointer blades. This procedure replaces the whole cutter assembly with a new one. A 480-V, 3-phase motor will be mounted on the side of the jointer housing, and a manifold to collect the chips will be constructed and incorporated into the existing dust-collection system.

**Stabilization Process Development:
Combustibles—Nitric Acid-Phosphoric Acid Oxidation**

Principal Investigator: Robert A. Pierce (Savannah River Site)

Task Description. This program will complete the development of a system for treating radioactive-contaminated organic materials. Savannah River Site (SRS) personnel will test and verify the applicability of the nitric acid-phosphoric acid oxidation system for combustible organic compounds contaminated with plutonium. Other associated tasks will develop a sensor for *in situ* monitoring of key compounds in the oxidation process, measure plutonium fractionation during operations, measure potential off-gas emissions, and verify the final immobilization of the resulting acid-metal mixture. Radioactive demonstration of the nitric acid-phosphoric acid process will complement nonradioactive pilot testing to be conducted in a Mixed-Waste Focus Area Program. Together, the two programs will essentially complete development of this system to treat Rocky Flats Environmental Technology Site combustible residues, SRS ^{238}Pu -contaminated organics, and other commercial nuclear wastes.

Status/Accomplishments. SRS personnel completed checking out the unit to run plutonium-bearing simulated waste compounds. Nonradioactive compounds have been processed. This work had been halted for a few weeks by manpower restrictions. Radioactive testing will

begin the week of April 14, 1997. The unit will be located in a radioactive hood in the Savannah River Technology Center.

Nonradioactive work was completed on iron phosphate glass to identify a glass composition to be used in immobilizing radioactive solutions. The glass uses 33% ferric oxide (Fe_2O_3), 5.5% sodium oxide (Na_2O), 2.5% strontium oxide (SrO), and 59% phosphorus pentoxide (P_2O_5). In other testing, researchers examined the range that can be used for processing the spent phosphoric acid solutions. The range for Fe_2O_3 is 20 wt %–40 wt %, Na_2O is 4 wt %–6 wt %, and SrO is 2 wt %–3 wt %.

Experimentation into identifying a suitable crucible for glass formation was initiated. In the first test, researchers looked at a porous, clay-bonded silica crucible. Static corrosion was less than expected, but dynamic corrosion was unacceptably high. Tests are in progress with a mullite-zircon (AZS) compound and a mullite material. Other tests will evaluate a more-dense clay-bonded fused silica, pure fused silica, and an alumina-silicon carbide compound. Follow-up work with a spectrophotometer has been conducted and results continue to look promising. Tests with high-temperature samples containing

dissolved iron have shown high potential for working *ex situ*. In such tests a small sidestream is withdrawn and diluted with a known amount of water. When tested this way, the instrument has shown an ability to measure to ± 0.05 M nitric acid (HNO_3). Experiments are under way to determine the effect of dissolved organics to see whether they create any measuring interference or bias. Samples have been generated with varying amounts of dissolved paper, plastic, and ion-exchange resin; these samples are ready to be tested.

Researchers have also begun work to look into using an autotitrator

instead of the spectrophotometer for measuring acid concentration. Initial testing has yielded encouraging results, but the technique is slower than that using the spectrophotometer. Additionally, the autotitrator will not measure iron or plutonium concentrations. However, this instrument can be considered as a back-up for HNO_3 because no interference from dissolved organics or any other light-absorbing compounds will occur. Availability of manpower has slowed progress with radioactive testing by a few weeks. However, testing will be initiated in April 1997 and will proceed according to the schedule.

***Stabilization Process Development:
Combustibles—Catalyzed Chemical Oxidation***

Principal Investigators: Wayne H. Smith

Charles Brown (Kaiser-Hill Company, Rocky Flats
Environmental Technology Site)

Task Description. The objective of this task is to demonstrate the catalytic chemical oxidation technology, specifically the DETOXSM process patented by Delphi Research Incorporated (DRI) of Albuquerque, New Mexico.

Status/Accomplishments. The contract work with DRI has been completed. A complete pilot-scale DETOX unit has been designed, assembled, and tested with

nonradioactive material. Also, in anticipation of introducing the system to a plutonium processing facility, two Los Alamos National Laboratory technicians, working along with DRI personnel, practiced installing the equipment in a mock-up glovebox. No future activities are planned for the project at this time. The equipment is currently in storage at DRI, pending implementation at either Los Alamos or at Rocky Flats Environmental Technology Site.

***Stabilization Process Development:
Combustibles—Pyrolysis of Polycubes***

**Principal Investigators: Daniel J. Kathios
John J. Coogan**

Task Description. Personnel at various sites in the Department of Energy nuclear complex cast plutonium and uranium oxides in a polystyrene matrix in order to perform criticality studies. Approximately 1600 polystyrene cubes in storage at Hanford Site now represent a waste that is not suitable for long-term storage. The aim of this work is to design, test, and deliver to Hanford a pyrolysis system that will effectively destroy and remove the polystyrene matrix, leaving the oxides as free-flowing powders that are suitable for either dissolution or long-term storage.

Pyrolysis is a pyrochemical technique whereby a high-temperature inert environment is used to break down and volatilize polymeric materials. Tests with nonradioactive materials have shown that the Los Alamos National Laboratory reactor design allows for almost 100% removal of the polystyrene without the formation of tars or other constituents that could adversely affect reactor operation. After pyrolysis is performed, an off-gas treatment technology is used to oxidize the organic constituents. Secondary combustion, catalytic conversion, and silent discharge plasma (SDP) are being considered for the treatment of the pyrolysis off-gas. Based on an engineering study prepared by Hanford, SDP has been

selected as the preferred option by Hanford personnel. Work will proceed toward logical hold points for all off-gas technologies until the technical maturity of the SDP can be demonstrated for this application.

Status/Accomplishments. We progressed as follows:

- We completed the hazards analysis for the polycube stabilization process using SDP as the off-gas treatment technology.
- We completed final design and procurement specifications for the secondary combustion off-gas treatment alternative.
- We fabricated two pyrolysis units. The two units will be used to supply real-time pyrolysis off-gas feed to the catalytic conversion and SDP pyrolysis off-gas treatment technologies.
- We completed the one-cell ceramic SDP unit test series.
- We completed the 6-cell ceramic SDP unit testing for the styrene and pyrolysis condensate feed streams. The test results indicated that a larger number of SDP cells would be needed to treat the peak off-gas flow rate from a pyrolysis unit loaded with 2-in. polycubes. The glovebox Hanford has for the

polycube stabilization system would prohibit a significant increase in the number of SDP cells. During the pyrolysis unit installation and check-out at Los Alamos with nonradioactive material, we conducted preliminary tests to determine whether the pyrolysis ramp rate could be slowed to reduce the peak off-gas. These preliminary tests indicated that the pyrolysis off-gas rate could be reduced at least 50%, and a comprehensive series of tests will be considered during the third quarter of fiscal year 1997. The six-cell SDP unit will be coupled with the pyrolysis unit for full-scale testing the first week of April 1997. This testing will generate data needed to design a prototype-production

unit for implementation at Hanford.

- Completion of the catalytic conversion system testing was postponed. The preheaters needed to complete the testing were received at Los Alamos, but they did not meet the requirements of the procurement specification. Appropriate preheaters will be fabricated by Los Alamos. The delay allowed investigation into the slower pyrolysis reactor ramp rate, which benefits all of the off-gas treatment technologies.
- Development of the polycube stabilization control system will resume when the off-gas treatment technology selection is finalized.

***Stabilization Process Development:
Combustibles—Washing***

Principal Investigators: Norman C. Schroeder and Moses Attrep, Jr.

Task Description. The objective of the organic wet combustible residue treatment is to test a proposed process flow sheet designed to remove organics and solvents and to stabilize finely divided plutonium metal contaminants from combustible residues.

Los Alamos National Laboratory researchers are also conducting experiments on nitrate-contaminated combustibles in order to test a proposed process flow sheet designed to remove by washing plutonium nitrate $\text{Pu}(\text{NO}_3)_4$ or plutonium oxide (PuO_2) from the combustibles with either water or 0.5 M potassium hydroxide (KOH). The washing process may be augmented by sonication, heat, or addition of detergent. This project is divided into two portions: working with cerium (nonradioactive) surrogates and experiments with plutonium-containing surrogates.

Status/Accomplishments.

Wet Organic Combustible Residue Treatment. We have completed the initial checkout of the Parr reactor, water injection system, and heating/cooling unit. The reactor was installed in a glovebox at the Los Alamos National Laboratory Radiochemistry Site, where it will undergo a final checkout procedure (Fig. 3).



Fig. 3. The Parr reactor installed in the glovebox in Alpha Wing, Los Alamos Radiochemistry Site, Building 1.

We have completed cerium reactions at full scale, 500 g of wet surrogate and 8% weight loading of the metal. Complete conversion of the cerium metal to the nonreactive state was confirmed by the hydrochloric acid (HCl) analytical method.

In February 1997, we were tasked with evaluating the reactor basket and the amount of water necessary to complete the steam oxidation step in the flow sheet. The evaluation of the reactor basket was completed, and the results were encouraging. The mesh size of the basket appears to be adequate to contain the surrogate material and to allow penetration of the steam, as indicated by the thermocouple embedded in the center of the surrogate material. Better control of the set-point temperature of 110°C by the cascade controller resulted in very little remaining melted surrogate adhering to the basket after the completion of the run. The amount of water necessary for the complete oxidation of the metal is 1 mL/g of surrogate. With the injection of the water at 90°C directly onto the side of the reactor vessel, the water is converted to steam and completely penetrates the surrogate within 10 min, allowing no delay in reaching the reaction temperature of 110°C. At the completion of the reaction, the reactor is vented to release the excess water vapor; and the surrogate is slightly damp to the touch. If additional drying of the surrogate is desired, heating of the

reactor while venting may continue or the basket may be removed from the reactor for air-drying.

The second week of April 1997 we will initiate plutonium experiments in the inert atmosphere glovebox. We will begin with small-scale reactivity experiments in the 300-mL Parr reactor.

Nitrate-Contaminated Combustible Residue Treatment. We completed the experimental plan for this flow sheet in March 1997, with approval by Safe Sites of Colorado, Rocky Flats Environmental Technology Site. Experiments with ^{141}Ce traced cerium ammonium nitrate $[\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6]$ in moderately concentrated nitric acid (HNO_3) to mimic the behavior of $[\text{Pu}(\text{NO}_3)_6]^{2-}$ sorbed onto the combustible materials. The experiments conducted on 1 g of dry surrogate show that >94% of the $[\text{Ce}(\text{NO}_3)_6]^{2-}$ can be removed from the combustibles with three 10:1 volume/weight (v/w) water washes. Experiments were conducted on both wet and dry ^{141}Ce loading, 0.5 M KOH washes, and on different amounts of water contact times. These experiments are illustrated in Fig. 4.

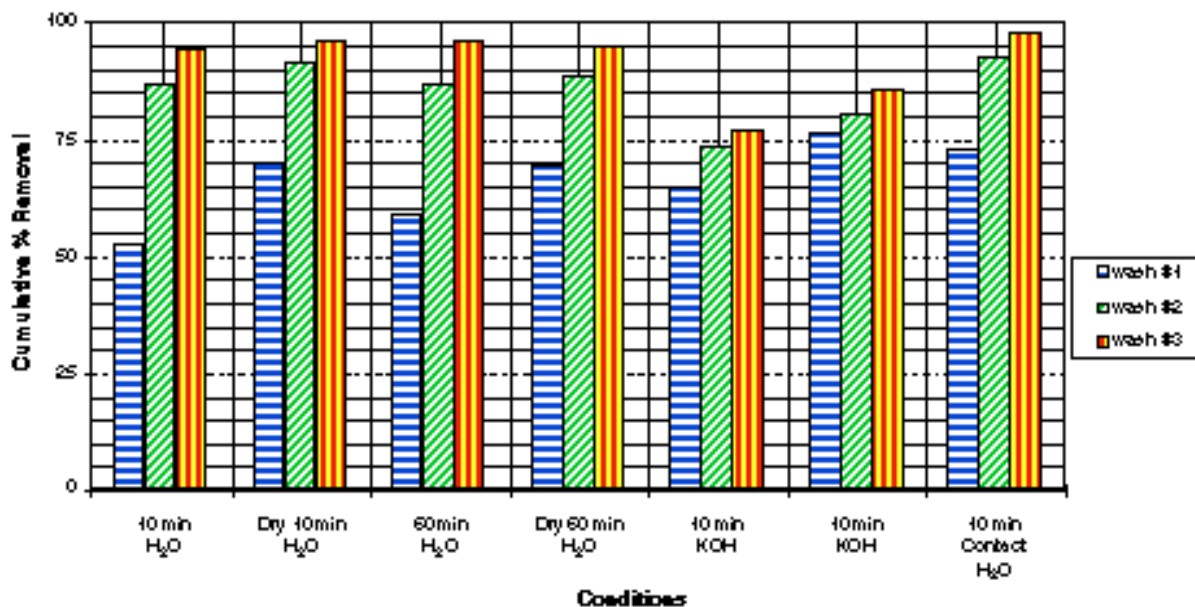


Fig. 4. Cerium nitrate removed from 1 g of surrogate.

Our plans are to scale up the dry surrogate material to 1/10th production scale. Experiments will be conducted using the 10:1 v/w water washes and ¹⁴¹Ce tracer. The feed

Type 1 (Full-Flo™ filter matrix) initial cerium experiments will be conducted to evaluate the removal of cerium oxide (CeO₂) according to the experimental plan.

***Stabilization Process Development:
Combustibles—Mediated Electrochemical Oxidation***

**Principal Investigators: Wayne H. Smith
Dean Kurath (Pacific Northwest National Laboratory)**

Task Description. Pacific Northwest National Laboratory (PNNL) researchers will complete two primary tasks to provide key design and engineering information required for implementation of the mediated electrochemical oxidation (MEO) process as a treatment of Rocky Flats Environmental Technology Site (RFETS) wastes. The first task provided support to the trade studies and rebaselining efforts for the treatment of plutonium-contaminated combustible wastes. The second task will involve development of a preconceptual design of a modified Catalyzed Electrochemical Plutonium Oxide Dissolution CEPOD II unit for treatment of contaminated filters.

Status/Accomplishments. The support to the trade study and RFETS rebaselining consisted of providing preliminary input on the treatment of plutonium-contaminated combustible wastes using the MEO process with a focus on the Full-Flo™ filters. In December 1996, PNNL personnel provided draft flow sheets for treatment of the filters and recovery of plutonium using precipitation and anion exchange, along with estimates

of liquid effluent volumes produced by MEO treatment.

The estimated liquid effluent for treating all of the combustible waste by MEO was nearly 75% lower than previous projections of 115 000 L. Table 2 shows the liquid effluent volume estimates for the plutonium anion-exchange and plutonium oxalate-precipitation flow sheets. The term recycle refers to the internal cycle of nitric acid solutions.

PNNL researchers will also develop a preconceptual design to treat the RFETS Full-Flo filters with a modified CEPOD II unit. This task begins April 1, 1997. They will identify key design and testing issues and provide a vision of a treatment system that may be implemented as an alternative to the existing baseline.

Anticipated design modifications to the existing CEPOD II system include incorporation of an anolyte recycle loop, reduction of the anolyte solution volume through resizing the separator, and incorporation of a filter housing into the process. PNNL will provide a draft report containing a preconceptual design of a modified CEPOD II unit by August 15, 1997.

Table 2. MEO Liquid Effluent Volume

Effluent Stream	Anion Exchange/ Pu(III) Oxalate Precipitation		Pu(III) Oxalate Precipitation	
	Without Recycle (L)	With Recycle (L)	Without Recycle (L)	With Recycle (L)
Catholyte	435	0	0 (to Anolyte)	0
Spent Anolyte	1 770	885	1 760	800
Filter Rinse	1 300	110	1 300	110
Neutralized Eluant	1 050	1 050	Not Applicable (NA)	NA
MEO Off-gas Scrub Solution	1 190	1 190	1 190	1 190
Total Filters Only	6 005	3 500	4 250	2 100
Total for All Waste	37 500	22 000	26 600	13 100

Ash:

Vitrification Issues with Rocky Flats Environmental Technology Site Ash and Sand, Slag, and Crucible

Principal Investigators: Gerald W. Veazey

Ronald K. Nakaoka

Mike Elliott (Pacific Northwest National Laboratory)

Task Description. The objective of this activity is to support the effort by Safe Sites of Colorado (SSOC) to develop a vitrified waste form for Rocky Flats Environmental Technology Site (RFETS) ash. The tasks are to determine nondestructive assay (NDA) restraints and operating parameters for a vitrified waste form and to investigate a conventional furnace system as an alternative to the RFETS microwave technology.

Status/Accomplishments.

NDA of vitrified waste forms. Several experiments were conducted at Pacific Northwest National Laboratory (PNNL) to determine the parameters for the preparation of the NDA sample. During these experiments, we discovered that significant foaming occurred during melting because of carbon off-gassing in the ash. When uncalcined ash was used, the surface of the melt rose as much as 52% over that of the unmelted ash/frit. This volume increase led to the need to decrease the initial ash/frit level to allow sufficient freeboard to contain the foaming. PNNL researchers found that precalcining the ash reduced foaming proportionally to calcination time and temperature. PNNL personnel also found that the Vollrath container, suggested for use by RFETS, experienced significant bulging and corrosion at 1100°C.

We prepared the NDA sample at Los Alamos National Laboratory at full scale using RFETS ash from the Los Alamos Plutonium Facility inventory. We used a low-temperature, borosilicate-based frit that melted at less than 1000°C. Before the ash was placed in the melt container, the ash was well blended with the glass frit in a V-blender. The melt container was an 88080 Vollrath can (8-in. diam), cut to 8 in. high to fit inside the furnace and inserted into a stainless steel can to address the corrosion and bulging problems identified at PNNL. We used a muffle furnace similar to that to be used at RFETS. We reduced the carbon content in the ash by calcining the ash/frit mixture in the melt container with a slow ramp up to 600°C over 12 h. We then melted the mixture by heating to 1000°C over an 8-h period and maintaining the temperature at 1000°C for 2 h. We cooled the waste form for approximately 18 h, at which time the center temperature was approximately 57°C. A post-melting inspection of the sample revealed no evidence of foaming.

It is the intention of RFETS personnel to use segmented gamma scanners (SGSs) with 1/2-in. collimators. The Los Alamos NDA study included SGS work with both 1/2-in. and 2-in.

collimators. This work was done to investigate end effects, i.e., the error effect that the edges of the sample have on the final assay. End effects are expected to be increased in the NDA sample because of the relatively large ratio of the size of even the 1/2-in. collimator to sample height. The 2-in. and 1/2-in. SGSs gave average values that were 34% and 17% low, respectively, compared to the initial plutonium assay by calorimetry. Lack of homogeneity of the plutonium within the sample is another factor that can decrease SGS accuracy. To determine the degree of homogeneity in this sample, we analyzed the sample using a tomographic gamma scanner (TGS). The results of the analysis of the NDA data for end effects and lack of homogeneity are still pending. Software correction techniques can be applied to compensate for error caused by end effects and lack of homogeneity.

In addition to the SGS and TGS studies, data was also collected using a thermal neutron counter (TNC). TNC techniques may be considered by RFETS if the error with the SGS is greater than 10% of calorimetry. The TNC is not susceptible to end effects and lack of homogeneity. However, it is susceptible to alpha-n reactions from such anions as chloride and fluoride, known to be at RFETS. The range of the plutonium content obtained from the TNC was +24% to -5% of the calorimetry assay. Correction techniques are available to compensate for alpha-n reactions if the anionic/alpha-n content is known.

Conventional Furnace Melting. The first milestone of obtaining surrogate compositions for RFETS ash and sand, slag, and crucible (SS&C) was met. However, because of a delay in transferring funding to PNNL, the next milestone of completing the computer modeling for the test design is only about 80% completed at this time. We have completed a literature search that has identified two candidate glasses that should be able to meet the RFETS need for a low-temperature glass. These candidate glasses are a borosilicate-based glass that melts in the 800°C–1000°C range and a vanadium/phosphate (V/P) glass that melts in the 600°C–800°C range. The borosilicate-type glass was successfully used to produce the full-scale NDA sample described previously. The V/P glass has been evaluated for its melting and encapsulation capabilities with crushed MgO crucible. The test showed the V/P glass had appropriate viscosity and easily flowed through the voids between the MgO particles.

In addition to demonstrating the proof-of-concept, the production of the full-scale NDA sample yielded valuable data for defining the operating parameters for the eventual full-scale process. Such information included cool-down rates for throughput calculations, temperature ramp-up rates for in-can calcination, and the effect of in-can calcination on foaming. Los Alamos, PNNL, and RFETS personnel, met March 27 for an information exchange aimed at development of the frit and a

flow sheet. Issues that were addressed included performance standards for the final glass form, process throughput goals, safeguards termination issues, and the ability at RFETS to calcine, blend, and grind the actinide

material. Guidance from this meeting has allowed completion of mass balance calculations and time-cycle analysis needed for flow-sheet development.

***Stabilization Process Development:
Ash—Vitrification of Rocky Flats Environmental Technology Site Ash***

Principal Investigator: Tracy S. Rudisill (Savannah River Site)

Task Description. Approximately 20 000 kg of incinerator ash are currently stored at the Rocky Flats Environmental Technology Site (RFETS). Vitrification has been proposed as one treatment technology to stabilize this material and produce a shippable waste form. Vitrification would allow shipment to the Waste Isolation Pilot Plant or potential disposal using the can-in-can approach with the Savannah River Site Defense Waste Processing Facility high-level waste glass.

The objectives of this work, currently being conducted at Savannah River Technology Center, are to demonstrate and optimize glass formulations and processing conditions required to vitrify the RFETS ash. Using the borosilicate and soda-lime-silicate glass formulations demonstrated during fiscal year 1996 (FY96) as the starting point, we are using a statistically designed experimental program to address the range of elemental compositions reported for RFETS ash and optimize the primary processing variables (liquidus temperature and viscosity) and glass durability. The program will consist of a series of melts during which the ash and/or frit composition is systematically varied to produce the most desirable processing conditions and glass durability.

Status/Accomplishments. We completed a 20-melt variability study to investigate the impact of the ash composition on the soda-lime-silicate glass. During the experiments, the concentration of key oxides [aluminum, calcium, chromium (III), copper (II), iron (III), magnesium, and sodium/potassium] were varied from low to high concentrations, while other components were held at their average values. We used hafnium and neodymium oxides in simulated ash as surrogates for plutonium and americium oxides respectively. Carbon, added as graphite, was removed by holding the furnace temperature at 900°C for 3 h. The melt temperature of 1350°C was then held for 4 h before pouring the molten glasses onto a steel plate. During the pour, a measure of viscosity based on an empirical scale and related to the fluidity of the glass was assigned to each formulation. The appearance of the glasses was also characterized by assigning a homogeneity rating of good, average, or poor.

Selected glasses were examined by x-ray diffraction in order to check for undissolved solids or crystallization. Each glass was x-ray amorphous. We then examined the same glasses by transmission electron microscopy (TEM). Results from the TEM show small (50–100 nm), round crystalline precipitates in opaque regions of the

glass. The glass with the poorest homogeneity contained the most crystals; however, the volume fraction was much less than 1%. No signs of amorphous phase separation were in any of the glasses. The composition of metal spheres produced, during three of the melts, from carbon reduction was determined by x-ray fluorescence. A copper-nickel alloy was identified, a finding which is consistent with the results from earlier melts and is the likely source of the crystalline precipitates identified with the TEM.

Implementation of a vitrification process at RFETS may be limited to temperatures below that required for fabrication of the soda-lime-silicate glasses. In response to this potential constraint, we initiated a parallel effort to develop a glass formulation with a processing temperature of 1000°C or

less. Initially, we fabricated an iron phosphate glass based on a low-melting iron(III)/phosphorous/sodium oxide ($\text{Fe}_2\text{O}_3/\text{P}_2\text{O}_5/\text{Na}_2\text{O}$) eutectic at 775°C using a 50-wt-% ash loading; however, metal oxides in the ash raised the melt temperature well above 1100°C. Acceptable borosilicate glasses, in terms of melting temperature and visual observation, were obtained by modifying a glass formulation proposed for high-sodium waste in tanks at Hanford Site. We obtained a 50-wt-% ash loading by removing refractory components (aluminum and zirconium oxides) from the frit and replacing them with boron and sodium oxides to reduce the melting temperature and viscosity. Characterization of the glasses is currently in progress.

***Surveillance and Monitoring:
Tomography***

Principal Investigator: Lynn A. Foster

Task Description. The aim of this project is to develop a noninvasive, nondestructive method for determining the contents and the condition of the transuranic (TRU) materials in containers currently being used. Our purpose is to eliminate unnecessary and unsafe handling of the packages and their contents.

Status/Accomplishments. Lawrence Livermore National Laboratory and Allied Signal, Inc., the two laboratories

who were contracted to acquire computerized tomography (CT) images on our CT phantoms, have begun to take data. Both laboratories expect to have completed their efforts by mid-April 1997. Once the data has been transmitted to Los Alamos National Laboratory, Los Alamos researchers will perform data analysis and image reconstruction and will write a report describing the results. The expected completion date for the report is May 30, 1997.

***Surveillance and Monitoring:
Moisture Probe***

Principal Investigator: Lynn A. Foster

Task Description. A neutron-based moisture probe will be field-tested at the Los Alamos National Laboratory Plutonium Facility (TA-55). Science Applications International Corporation (SAIC) is currently developing a bench-top model for nondestructive analysis of moisture content in plutonium oxide packages. This bench-top model will be delivered to Los Alamos and tested using plutonium oxide (PuO_2) with known moisture content that is sealed in long-term storage containers. For this study, plutonium oxide standards will be produced and characterized by Los Alamos personnel. These standards will have moisture contents that bracket the 0.5 mass % required for long-term storage of PuO_2 . The applicability of neutron-moderation techniques for quantification of PuO_2 moisture content at or below the 0.5-mass-% level will be evaluated in this project.

Status/Accomplishments. SAIC personnel are continuing with the feasibility study and production of a bench-top model neutron probe for

nondestructively verifying the moisture content of plutonium oxide destined for long-term storage. SAIC researchers asked for and were granted a no-cost contract extension until April 18, 1997, for completion of this study. Preliminary measurements on surrogate materials at SAIC suggest the minimum detection limits will be <0.1-mass-% moisture, well below the 0.5-mass-% criteria for long-term storage. When preliminary tests at SAIC are completed, the bench-top unit will be field tested at TA-55. Performance of the bench-top model will be tested against the standard loss-on-ignition (LOI) test for moisture determination.

Los Alamos is currently in the process of producing two standards for use in the field test of the bench-top model moisture probe. One standard will contain approximately 1.5-mass-% water, and one will be near the long-term storage criteria of 0.5 mass %. Los Alamos currently has several cans of plutonium oxide in storage that have very low LOIs, <0.05 mass %. These items will be used for baseline measurements in the field test.

***Surveillance and Monitoring:
Acoustic Resonance Spectroscopy***

Principal Investigator: D. Kirk Veirs

Task Description. The objective of this project is to develop a noninvasive, nondestructive method for monitoring increases in gas pressure and changes in gas composition within sealed storage containers. The method, using acoustical excitation and detection, is based on measuring the properties of standing waves produced in a gas contained within an acoustic cavity. The frequency of the standing waves changes with gas composition, and the intensity changes with gas pressure.

Status/Accomplishments. The effect of gas composition on line position and line width was studied by Los Alamos National Laboratory researchers. We built a new gas-handling manifold that allows accurate gas mixtures to be prepared. These gas mixtures were studied in a spherical acoustical cavity. The spherical cavity was used because the theory for acoustic response is better understood for the sphere than

for the storage container. Spectra showed changes in line positions from positions predicted by theory. The differences between our experiments and theory were especially prominent in gases containing carbon dioxide. The lack of agreement has prompted us to check the purity of the gases that we used to prepare the gas mixtures. The line widths definitely changed as the gas composition changed. This information was quantified by fitting the observed spectra. The line widths provide additional information for identifying composition of the gas.

The design of the inner storage can that is to be used at Los Alamos has been refined. A storage can with the new design will be obtained, fitted with a cylindrical cavity, and tested using a variety of gas mixtures. The ability to observe and quantitatively interpret gas modes using the new container design will be studied.

***Surveillance and Monitoring:
Nondestructive Assay—Gamma Salts***

Principal Investigator: Teresa L. Cremers

Task Description. This activity provides a means to analyze heterogeneous plutonium- and americium-bearing salts for plutonium isotopic distribution and americium concentration.

Status/Accomplishments. Work on plutonium (and uranium) isotopic analysis is proceeding on two fronts. First, we are developing a physics-based model for the relative efficiency curve with the intent of replacing the empirical model currently being used. A test version of this new model has been programmed and tested on several types of spectra, including spectra from the Los Alamos National Laboratory Plutonium Facility (TA-55). This new relatively efficient model is continuing to be tested and is planned for incorporation in version 3 of the plutonium gamma ray isotopic

analysis code, personal computer Fixed energy Response function Analysis with Multiple efficiency (PC/FRAM), in use at TA-55.

We are completing the documentation and acceptance of versions 2.2 and 2.3 of PC/FRAM. We will next start on version 3 with full 32-bit capability. This task requires us to work with some new development tools and make extensive modifications to the software libraries of the Los Alamos Nonproliferation and International Security Division Safeguards Assay Group. Besides incorporating the new relative efficiency function discussed above, we will also incorporate an initial version of automated parameter file selection. This latter development will be particularly useful for improving the automation of residue measurements.

***Surveillance and Monitoring:
Calorimetry***

Principal Investigator: Teresa L. Cremers

Task Description. Researchers on this task are applying finite element analysis to obtaining a model that will predict calorimeter performance and permit the design of smaller, faster calorimeters.

Status/Accomplishments. Los Alamos National Laboratory researchers have ordered and received the integrated design tool I-DEAS™ by Structural Dynamics Research Corporation. We are upgrading a desktop machine to

permit the I-DEAS tool to run efficiently. The upgrade includes a large fast disk, additional memory, and an enhanced video display adapter. The design tool has been installed on the machine, and now we are beginning the learning curve to use the tool. The tool will be used to develop 3-D models and generate the mesh for them. The thermal modeling will be performed using the ABAQUS™ package.

***Surveillance and Monitoring:
Risk Status of Residue Holdings at Rocky Flats Environmental Technology Site***

Principal Investigator: Thomas L. Rising

Task Description. The purpose of this task is to assess the risk status of Rocky Flats Environmental Technology Site (RFETS) residue holdings described in the Defense Nuclear Facilities Safety Board (DNFSB) Recommendation 94-1. At issue is the change in risk status during the past three years. This change resulted from effects of aging and from mitigation efforts, such as drum venting and repackaging. The analysis will address both the status before DNFSB 94-1 remediation efforts and the current status and will provide information needed in the development of methodologies for predicting future risk behavior. These methodologies will be based on various program scenarios.

Status/Accomplishments. The Los Alamos National Laboratory research team is employing a phenomenologically based probabilistic approach to estimate the time-dependent probability of both chronic and energetic drum failures. Insufficient data were available for performing a conventional risk analysis. Sound engineering logic was employed with boundary conditions coming from sampling data. An outside subject-matter expert, Dr. William Averill of the Colorado School of Mines,

was brought in to critique the analysis, which was then modified.

The analysis suggests that the probability of an energetic drum failure has been reduced by a factor of 50, through venting and stabilizing activities. However, the probability of a chronic drum failure increased 15% in the same three-year period of time.

Armed with 115 data points from the RFETS residue sampling plan, the team evaluated several different approaches to the risk assessment. The data were of uneven quality and, for the most part, failed to capture all the relevant attributes of package containment failure. The team did not have sufficient information to employ traditional methods of risk assessment. Furthermore, these methods are particularly weak in quantitatively evaluating time-dependent differences in estimated risk. Therefore, Los Alamos researchers assembled a set of probabilistic engineering estimates for the types of failure that RFETS and DNFSB personnel had previously identified.

The Los Alamos team traveled to RFETS and briefed the project principals on the approach and asked for feedback and suggestions. The approach was well received and the

team proceeded to update the analysis. The approach was implemented and final estimates of risk were developed. The team returned to RFETS and gave the final briefing. Again it was well received.

Development of the plan for in-depth assessment of risk status, containing resource and information requirements, and the final report about the risk work will be complete at the end of April 1997, on schedule.

Core Technology:**Actinide Solution Chemistry in Residues and in Residue Stabilization and Treatment Processes****Principal Investigator: John M. Berg**

Task Description. Los Alamos National Laboratory researchers on this project seek to describe aspects of the solution chemistry of actinide elements in legacy residues and in proposed residue treatment processes. Our findings are intended to guide stabilization and disposition decisions and to enable efficient optimization of treatment processes.

Status/Accomplishments. Analysis of Pu(IV) solution spectroscopic data in high-ionic-strength acidic nitrate solutions acquired over the past 12 months was partially analyzed

during the second quarter of fiscal year 1997 (FY97). We deconvoluted the full set of nitric acid spectra for each of 10 different ionic-strength series. From these spectra we obtained overall formation constants for the first two Pu(IV) nitrate complexes, as a function of ionic strength, from 2 mol/kg to 19 mol/kg, greatly extending the quantitative information on this system. A plot of these formation constants is shown in Fig. 5. We will present these results at two external scientific meetings in the third quarter of FY97.

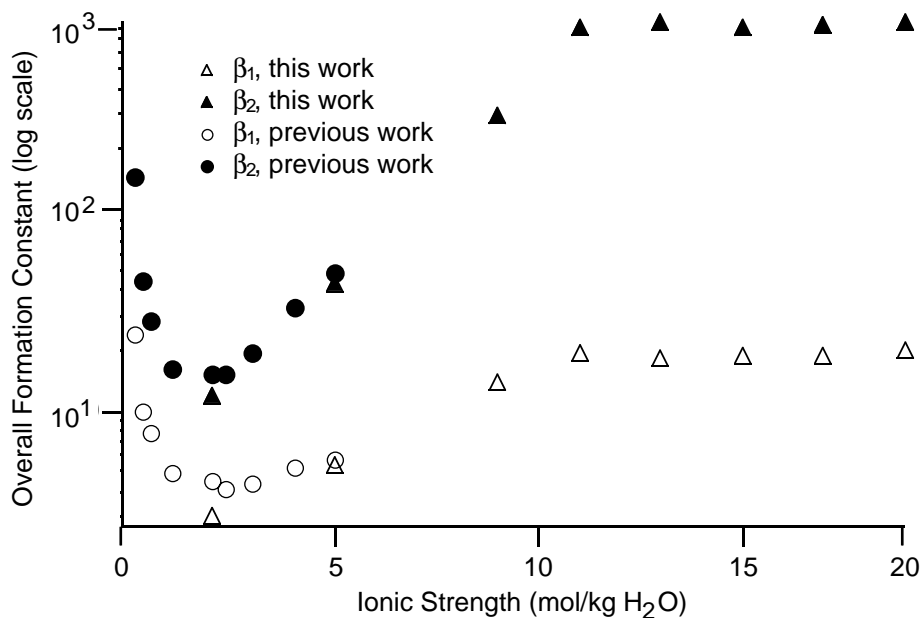


Fig. 5. Ionic-strength dependence of overall $\text{Pu}(\text{NO}_3)_3^{3+}$ and $\text{Pu}(\text{NO}_3)_2^{2+}$ formation constants compared with earlier work.

Our next goals of the nitrate data analysis efforts are to produce similar formation constant determinations for the higher complexes in which three or more nitrates are bound to the Pu(IV) ion. We have also begun analysis of data on the Pu(IV) chloride system, and this analysis will continue in the third quarter of FY97. We also plan to conduct additional experiments on the chloride system and to begin fluoride experiments in the third quarter.

We prepared plutonyl carbonate (PuO_2CO_3) by bubbling carbon dioxide through a stirred acidic stock solution

for 3–5 days, washing the resulting precipitate with distilled deionized water, redissolving, and repeating precipitation. Ozone was also bubbled through the suspension for the final 2 days to reoxidize any plutonium reduced by radiolysis. We characterized the resulting pale tan solid using powder x-ray diffraction (Inel, CPS-120) (See Fig. 6), extended x-ray absorbance fine-structure (EXAFS) spectroscopy, and diffuse reflectance spectroscopy. The PuO_2CO_3 preparation and characterization has been reported and submitted for publication.¹⁻³

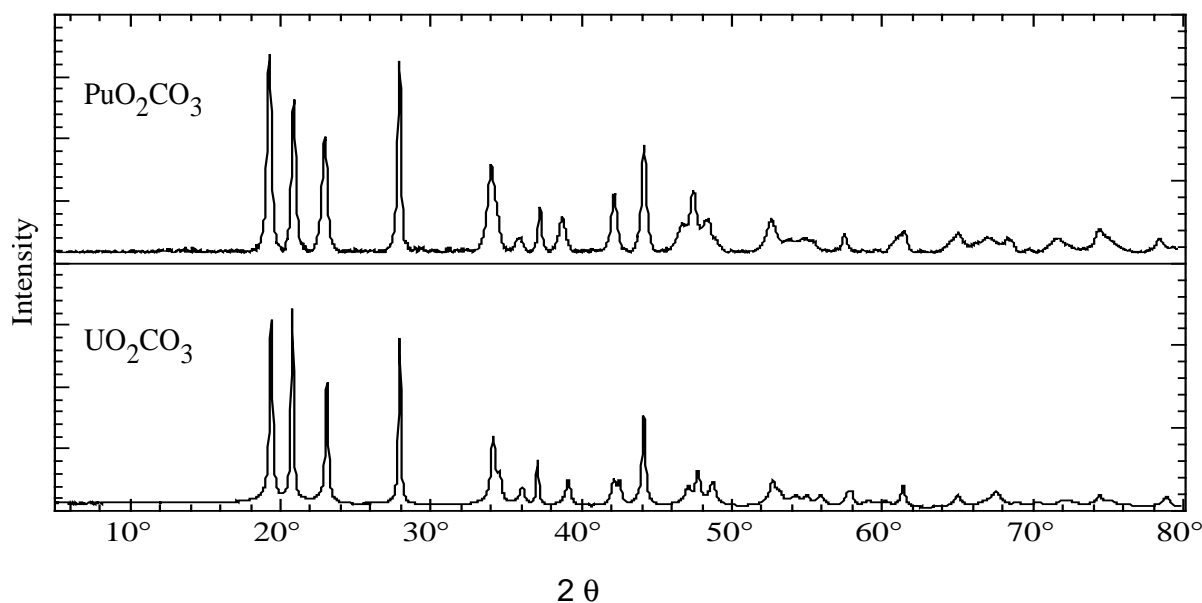


Fig. 6. Powder x-ray diffraction of plutonyl carbonate compared with uranyl carbonate.

The molecular and solid-state structure of $\text{Pu}(\text{CO}_3)_5^{6-}$ was determined using single-crystal x-ray diffraction and solution EXAFS spectroscopy (funded equally by the DOE Office of Basic Energy Sciences and the 94-1 R&D project). The ultraviolet-visible

near infrared (UV-VIS-NIR) solution, diffuse reflectance of single crystals, and EXAFS solution spectra show that the same anion is present in both solution and the solid state. The nature of this complex has been in debate for almost two decades.

References

1. M. P. Neu, S. D. Reilly, and W. H. Runde, "Plutonium Solubility and Speciation to be Applied to the Separation of Hydrothermal Waste Treatment Effluent," to be published in *Materials Research Society Symposium Proceedings Series, II. Scientific Basis for Nuclear Waste Management XX*, Volume 465.
2. W. H. Runde, C. Lierse, and B. Eichhorn, to be published in *Geochim. Cosmochim. Acta*.
3. P. D. Palmer, D. L. Clark, et al., unpublished results.

Core Technology:***Chemical and Physical Interactions of Actinides with Residue Substrates***

Principal Investigator: David E. Morris

Project Description. Focus of this project is on molecular spectroscopic characterization of the interaction of plutonium and other actinides with several important residue classes and eventually, with stabilized materials. The residue classes to be included are combustibles (ion-exchange resins and cellulosic materials) and incinerator ash.

Status/Accomplishments. The project principal investigator from Los Alamos National Laboratory made technical presentations at both the internal and external core technology program reviews held during this reporting period. Both presentations were very well received. Our postdoctoral research fellow began work on the project February 24, 1997; however, security clearances have been restricted by DOE and this person currently is unable to work without an escort and supervision in the laboratory. This inconvenience could impact productivity. Abstracts describing our research on this project have been submitted for the national American Chemical Society meeting in Las Vegas, Nevada (September 1997) and the Plutonium Futures—The Science topical conference in Santa Fe, New Mexico (August 1997).

Research Highlights. We obtained the first x-ray microfluorescence elemental plutonium maps of Rocky Flats Environmental Technology Site ash residue on two separate sample preparations. One sample was a bulk powder using a 100- μm aperture. The second sample was a thin film fixed with a dilute solution of white glue and a 300- μm aperture. The 300- μm aperture was necessary to obtain sufficient x-ray intensity. Shielding of the detector was necessary to decrease radiation burden. More than eight elements were successfully mapped. The maps illustrated the extreme heterogeneity of the ash residue.

During the second quarter of fiscal year 1997, Los Alamos researchers conducted a series of experiments to quantify the nitric acid (HNO_3) washing of Pu(IV) from freshly loaded Reillex HPQTM anion-exchange resin as a function of acid concentration. These experiments were aimed in part at determining the factors leading to residual plutonium on washed resins and in part at studying the loading and washing kinetics with the goal of improving our understanding of the mechanisms of plutonium-resin binding. Our results show that plutonium is washed least efficiently by a concentration of 8-M HNO_3 and that, as expected, washing becomes

much more efficient as HNO_3 concentration is decreased. Some deviation from loading/washing reversibility was noted at acid concentrations higher than 8 M, when less plutonium washed off than the loading studies might lead one to expect.

We initiated photoacoustic spectroscopic measurements of plutonium bound to aged samples of both Dowex 11TM and Reillex HPQ resins. The HNO_3 aging process for these samples began January 3, 1997, and will be ongoing for at least one year. The spectral acquisition has been temporarily delayed by laser system problems that will be corrected. We also are continuing by Raman spectroscopy to acquire spectral data on the aging resin samples in order to assess the effects of aging. We hope to have a full year of aging data to allow us to prepare a manuscript on these

effects. Most recently, we used luminescence spectroscopy to re-examine 6-months-old samples of uranium-loaded resins.

We will compare these new results with those collected last summer in order to look for changes in modes of interaction. Finally, we spent considerable time and effort searching the literature and assimilating existing information on two current 94-1 R&D program issues: nitration of residue materials to generate potential explosion hazards and a simple means to determine the thermal emittance of DOE standard 3013-96 containers and their contents. Technical reports on both paper studies will be forthcoming. The thermal emittance measurement issue has been resolved, and soon a proposal will be made to the material identification and surveillance project.

Core Technology:***Identification and Characterization of Changes in the Chemical State of Plutonium in Interim Waste Forms*****Principal Investigator: D. Kirk Veirs**

Project Description. The purpose of this work is to identify and characterize changes in the physicochemical state of plutonium compounds found in residues. The techniques also will be applied to stabilized materials. Plutonium-containing materials other than metal and pure oxide are being studied using x-ray diffraction (XRD, powder, and single-crystal), x-ray absorption spectroscopy (XAS), x-ray photoelectron spectroscopy (XPS), and optical spectroscopies (reflectance, absorption, and Raman) to identify changes in the local chemical environment of the plutonium metal center. Changes in the local chemical environment can indicate the onset of deleterious transformations in the waste form that may lead to unsafe storage conditions.

Status/Accomplishments. During the second quarter of fiscal year 1997, Los Alamos National Laboratory researchers examined samples from the January 1997 experimental run at Stanford Synchrotron Radiation Laboratory (SSRL). These samples include well-characterized plutonium carbonate species, a plutonium metal standard for calibrating the x-ray absorption near-edge structure

(XANES) data, and a residue sample of spent ion-exchange resin that had been stored for many years in a steel canister.

The XANES and extended x-ray absorption fine-structure (EXAFS) data for the residue sample of spent ion-exchange resin were partially analyzed. The results indicate that the plutonium is mainly in the IV oxidation state, and the distances of nearest neighbors are consistent with polymeric-like plutonium. There did not appear to be any nearest neighbors at the distances where bound chloride is observed normally. The sample was from a resin originally used in the chloride process at the Los Alamos Plutonium Facility and contained enough hydrochloric acid to completely corrode the steel can it was stored in. It was surprising that the plutonium did not seem to be coordinated to chloride. The plutonium that originally passed through the resin was in hydrochloric acid and was not polymeric. Is the polymeric plutonium found on the aged resin a result of aging? The data from this run will be analyzed further.

Samples of resin from separations columns currently in operation will be examined in order to determine a hard-to-wash-off form of plutonium that is associated with the resin. Samples of

resins used in both the hydrochloric acid and nitric acid processes will be examined. The results when compared to each other and to the results for the aged sample will allow us to determine whether polymeric, like

plutonium species, occur readily on resins or if that form of plutonium is produced by aging. Such results will help to define appropriate methods for separating the plutonium from the resin.

**Core Technology:
Corrosion**

Principal Investigator: Darryl P. Butt

Task Description. Los Alamos National Laboratory researchers are incorporating two agendas in their current corrosion studies. The primary thrust is the examination of the effects of crystallographic orientation on the electrochemical behavior of engineering materials relevant to the 94-1 R&D project. In our experiments we will couple localized corrosion measurements with orientation imaging microscopy. We will focus the second portion of our efforts on the effects of crystallographic texture on stress-corrosion cracking of materials.

Status/Accomplishments. Research for the 94-1 R&D project core technology corrosion effort was on schedule for the second quarter of fiscal year 1997 (FY97). We are coupling localized corrosion measurements (using a scanning electrode technique) with crystallographic orientation mapping of surfaces (using orientation imaging microscopy [OIM]). On a fundamental level, the goal of this research is to understand the effects of crystal structure on pit initiation and to gain insight into the stochastic nature of pitting. On an applied level, our objective is to produce recommendations for developing processing means that promote

corrosion resistance of engineering materials.

In the initial stages of this work, we are focusing on the production of model materials suitable for study. The study of model materials is a necessary precursor to the study of engineering materials. Materials design, production, and modification are required to yield model materials that are suitable for study because these materials are not commercially available. This portion of the research is one of the most difficult and time-consuming portions of the research plan. Research in the first quarter of FY97 focused on the production of polycrystalline nickel, single-crystal nickel, and stainless-steel (SS) materials. An initial batch of polycrystalline nickel was produced by powder metallurgy. Material fabricated from powder is required to produce randomly oriented grains. A surface composed of randomly oriented grains will enable an examination of all possible crystallographic orientations. Nickel with randomly oriented surface grains is not commercially available because the processing history of the metal from production invariably results in surfaces having a predominance of one or more particular orientations. The initial powder metallurgy run produced

material that was insufficient for electrochemical study because of incomplete densification during hot

isostatic pressing (Fig. 7). Production parameters have been altered and a second run is currently under way.

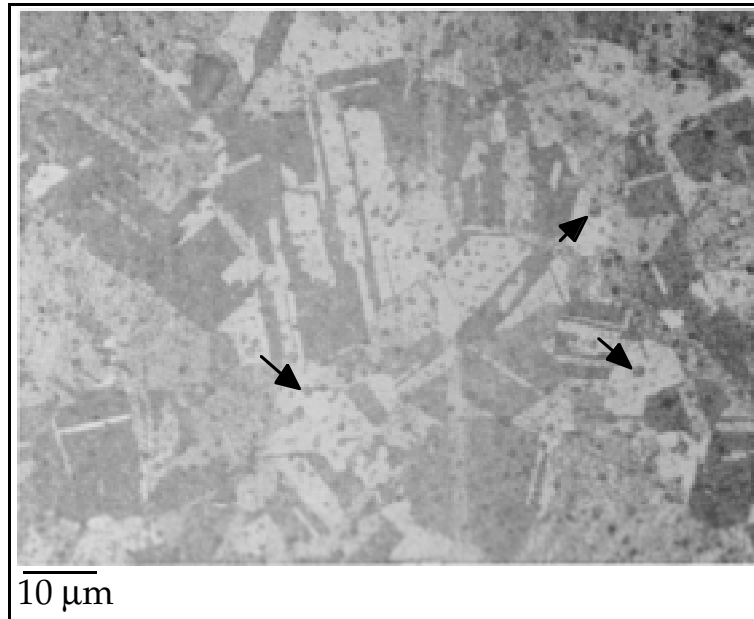


Fig. 7. Polycrystalline nickel samples produced by powder metallurgy. Arrows indicate selected pores resulting from incomplete densification.

Additionally, the methodology for producing single crystals of nickel is currently being refined. Initial crystals produced by the optical-floating-zone method resulted in materials that were unsuitable for use because of the incorporation of inclusions (Fig. 8). Alterations to the atmosphere during crystal growth appear to have alleviated this problem, although a more rigorous analysis using a variety of techniques is required. The analysis

should be completed early in the third quarter of FY97. If the material proves suitable for use, electrochemical testing of the material will commence. Finally, design of SS materials is also ongoing. Current work involves experimental heat treatments of 304 SS to optimize grain size while avoiding sensitization and thermal etching. This work should be completed during the third quarter of FY97.



Fig. 8. Nickel, single-crystal (100). Arrows indicate oxide inclusions.

In addition to materials production, electrochemical studies were performed during the first quarter of FY97. Previous work has indicated that crystallographic pitting is observed following immersion of 304 SS in 4.1 M nitric acid (HNO_3) + 1 M sodium chloride (NaCl). More specifically, crystallographic pitting is observed following the sequence of (1) active dissolution concurrent with autocatalytic reduction of nitrogen-based cathodic reactants (NO_3^- , NO_2^- , NO) in solution, (2) spontaneous passivation arising from anodic polarization caused by autocatalytic reduction, (3) localized chemistry formation resulting in crystallographic pitting. This sequence presents problems for the OIM work to be used in conjunction with electrochemical tests for the following reasons. OIM cannot be performed

ahead of immersion because the grain orientations that populate the surface before immersion will entirely dissolve, resulting in new, different surface grains to undergo pitting. OIM cannot be performed after dissolution because OIM requires a planar surface, whereas dissolution results in a sharply faceted surface. Thus, a technique must be developed to produce crystallographic pitting of 304 SS without dissolution. Such a technique is currently being investigated. Alterations in solution chemistry by means of gaseous reductant and metal salt additions are currently being explored.

An OIM has been received and assembled at Los Alamos. The system is currently being calibrated. Initial OIM runs on SS are planned for the third quarter of FY97.

A special electrochemical cell for scanning reference electrode testing was tested in the second quarter of FY97. Modifications to optimize the cell continued during the second quarter. A patent disclosure was filed during the quarter in an initial step to patenting the design.

In addition to our experimental electrochemical studies, we have also performed thermodynamic calculations to assess whether or not SS containers intended to be used for nuclear material storage might be susceptible to gallium embrittlement. Gallium is present in weapons-grade plutonium in concentrations on the order of 1 wt %. Preliminary thermal

transport calculations performed by the Los Alamos nuclear systems design and analysis group suggest that temperatures in the containers could reach 600°C locally. Preliminary thermodynamic calculations (shown in Fig. 9) indicate that in an inert atmosphere the gallium concentrations would be quite low and should not be an issue. However, if hydrogen concentrations could build up in the system because of reactions between residual water vapor and metals, Ga_2O_3 could be reduced to $\text{Ga}_2\text{O}(\text{g})$. Further calculations are necessary to determine whether we need an experimental effort to look at this issue in greater detail.

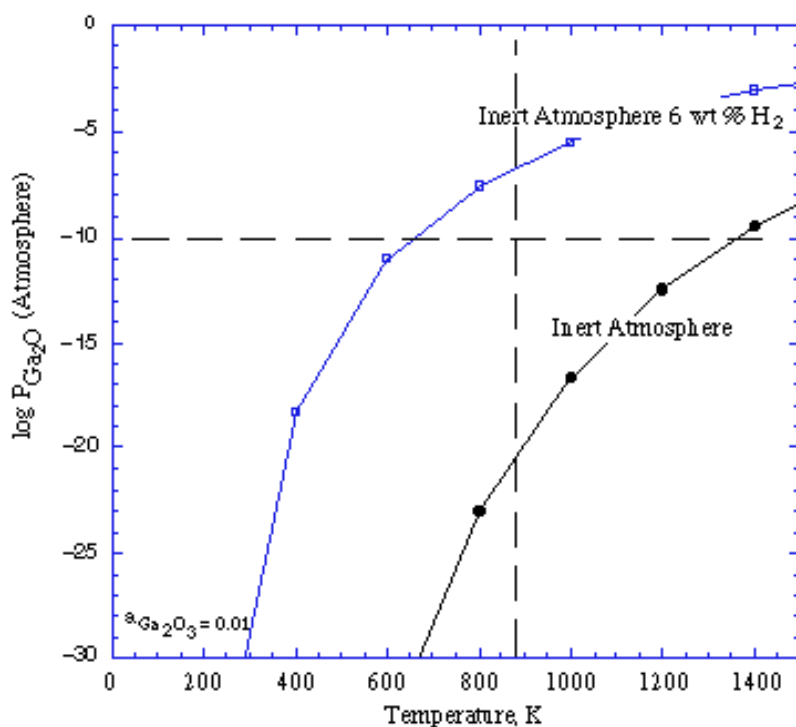


Fig. 9. Calculated equilibrium partial pressure above a waste containing Ga_2O_3 with an activity of 0.01.

Recent Publications

1. D. G. Kolman, D. K. Ford, D. P. Butt, and T. O. Nelson, "Corrosion of 304 Stainless Steel Exposed to Nitric Acid-Chloride Environments," accepted for publication in *Corrosion Science*, 1997.
2. D. G. Kolman, D. K. Ford, D. P. Butt, and T. O. Nelson, "Corrosion of 304 Stainless Steel Exposed to Nitric Acid-Chloride Environments," CORROSION/97 conference, paper no. 125, National Association of Corrosion Engineers, Houston, Texas, 1997.

**Core Technology:
Separations—Polymer Filtration**

Principal Investigators: Gordon D. Jarvinen
Barbara F. Smith

Task Description. Polymer filtration removes actinides to very low levels from solutions to meet site-specific liquid discharge requirements. The objective of this task is to develop the underlying science and optimize the polymer filtration process for potential 94-1 R&D project application.

Status/Accomplishments. Efforts of Los Alamos National Laboratory researchers in the second quarter of fiscal year 1997 have primarily been focused on the laser luminescence component of the research project. Tasks initiated and completed this quarter relative to this work include the following:

- We synthesized and prepared the dimethylaminomethylene diphosphonic acid (DMAMP) model ligand/metal complex.
- We characterized DMAMP by thermogravimetric analysis, elemental analysis, and laser luminescence.
- We prepared europium-doped DMAMP (model ligand), polyethyleneamine (base polymer), and MP996 (diphosphonic acid water-soluble polymer) for laser luminescence interrogation.

- We determined inner-sphere coordinated H_2O by lanthanide ion probe spectroscopy.
- We obtained by laser luminescence time-resolved and spectral signature (fluorescence absorption) measurements of europium-doped DMAMP, polyethyleneamine, and MP996 diphosphonic acid water-soluble polymer at multiple pH points.
- In April we presented a report on this work in Hawaii at the Fourth International Conference on Methods and Applications of Radioanalytical Chemistry.

A summary of the results from these investigations are as follows:

- We identified discrete binding environments as a function of polymeric chelating agent and operational pH.
- We determined 1:1 DMAMP model ligand inner-sphere coordinated H_2O to be 1, and this determination was confirmed by thermogravimetric analysis.
- We determined that the 1:1-DMAMP model ligand was *not* representative of MP996 chelating polymer primary binding environment.

- 5D_0 - 7F_0 absorption spectra and time-resolved measurements by lanthanide ion probe spectroscopy (LIPS) look promising as a diagnostic tool for the characterization of water-soluble polymers.

Our current and future efforts are planned as follows:

- We will develop further model ligand/metal complexes to serve as reference materials for MP996 and other water-soluble polymers. (See Fig. 10)
- We will expand our study to include other water-soluble polymers of interest, e.g., carboxylate- and hydroxamate-containing polymers.
- We will expand experimental protocol to include luminescence measurements at more pH points.
- We will incorporate energy-transfer, fluorescence saturation, and cryogenic experiments.

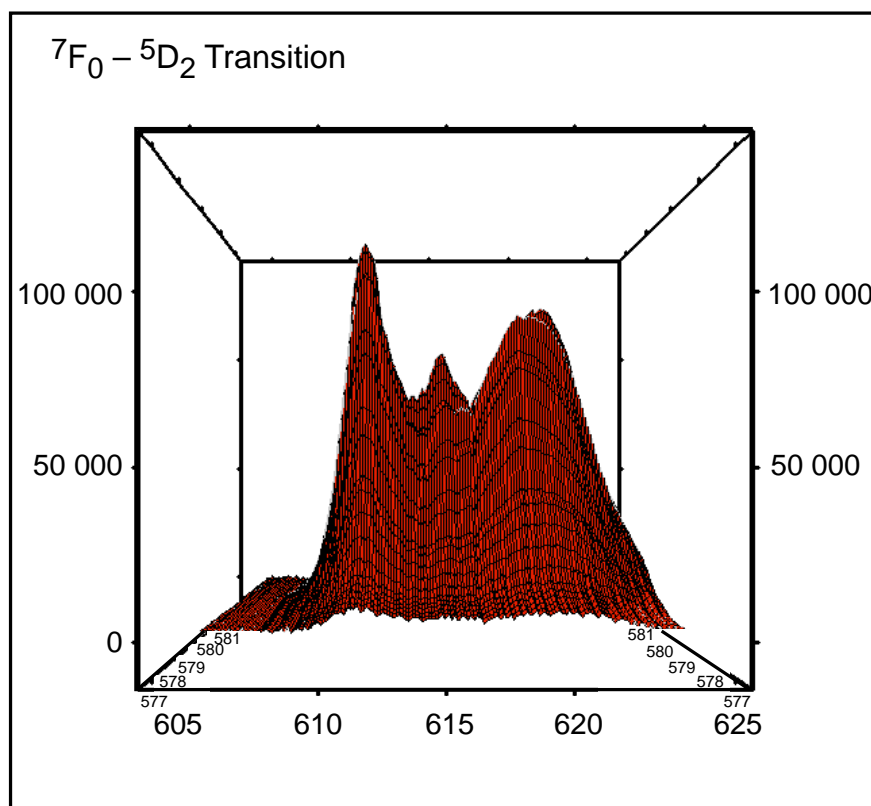


Fig. 10 (a). Spectral signature measurements by LIPS for DMAMP model ligand.

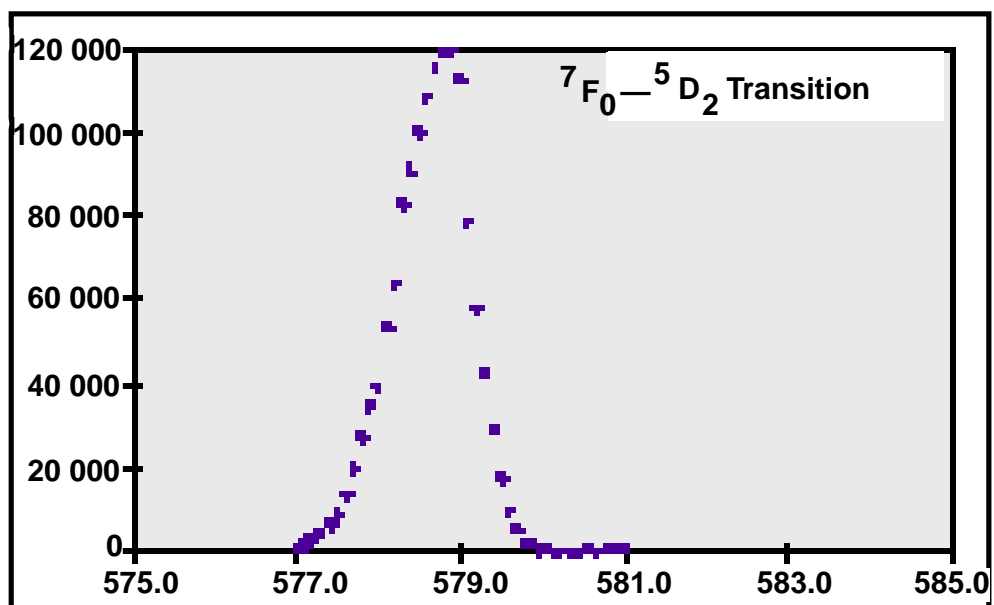


Fig. 10 (b). Absorption measurements by LIPS for DMAMP model ligand.

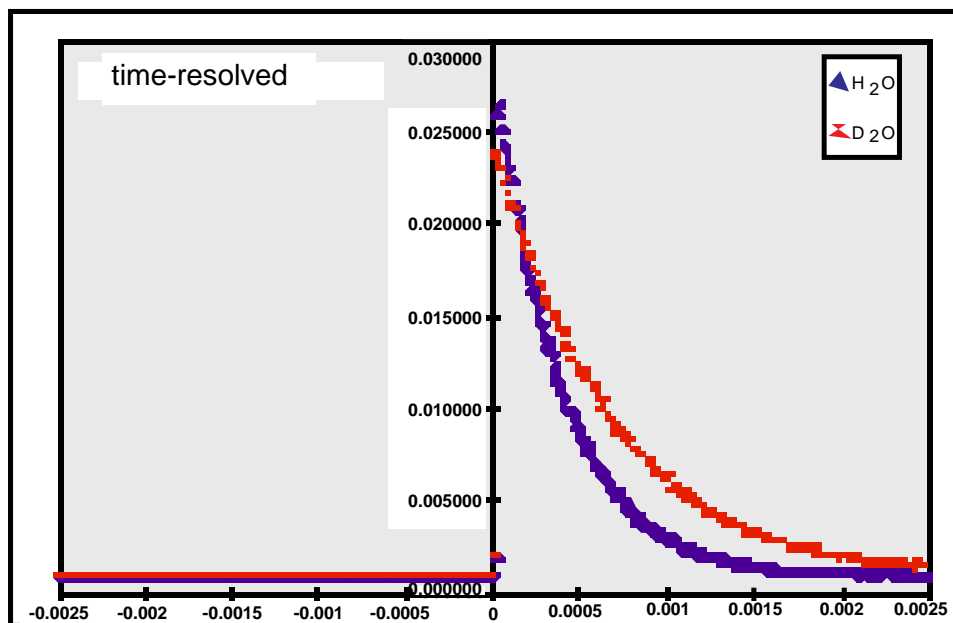


Fig. 10 (c). Time-resolved measurements by LIPS for DMAMP model ligand.

Core Technology:
Separations—Polymer Foams

Principal Investigators: Gordon D. Jarvinen
Betty S. Jorgensen

Task Description. Los Alamos National Laboratory researchers are investigating metal uptake, using polymer foams for potential 94-1 R&D project application. The foams may offer an improved alternative to resin beads. Foams containing graft-polymerized ligands are being compared to resin beads with similar ligands for metal uptakes.

Status/Accomplishments.

Plutonium Uptake Studies. We determined distribution coefficients for plutonium uptake for foams with three different levels of polyvinylpyridine (PVP) grafting. K_d determinations for Reillex™ 425 will be completed soon for

comparison with the metal uptake on the foams. The kinetics in our plutonium uptake studies were not as fast as anticipated. Possible explanations are that the vinylpyridine chains may be assuming undesirable configurations for fast complexation because of the requirement for two binding sites or that the chains may be experiencing stiffening upon binding plutonium. The solution may be to include flexible spacer groups through copolymerization with other monomers. A synergistic effect can also be achieved by including coligands in the chain by including vinylphosphonate in the vinylpyridine chain, as we observed earlier.

Table 3. Plutonium Uptake Studies

Sample wt% Grafted PVP	30 min Kd	2 hr Kd	6 hr Kd
194	48	160	842
92	63	106	224
29	2.2	7.3	8.2

Foam Capacities. The foam capacity of the 194%-weight-gain sample for iron uptake from 10-N hydrochloric acid (HCl) was slightly higher than the iron capacity of the resin-beads under similar conditions. The foams with lower amounts of grafting have lower capacities, as expected, when the capacity is determined on a total

weight basis. If the capacity is determined based on the amount of grafted PVP, the capacity is higher but tends to decrease as the percent of grafting decreases. The foams with higher percent of grafting would be expected to have longer chains. This result may indicate that the longer chains are more efficient in binding

iron. PVP chains have a theoretical capacity of 9.51 meq/g, assuming a

1:1 ratio of metal ion to ligand. The results are shown in Table 4.

Table 4. Foam Capacities

Sample (Weight Gain)	Total Weight (meq/g)	Grafted PVP Only (meq/g)
194%	4.45	6.75
144%	3.81	6.47
109%	3.26	6.25
92%	2.29	4.77
88%	2.68	5.73
Reillex 425	4.04	

University Contract. Spiro Alexandratos, University of Tennessee, is the author of this section of the report.

Foams received from Los Alamos were prepared and characterized for functionalization at the university. Initial studies with the 75:25 vinylbenzyl chloride:styrene foam focused on reaction with methylene diphosphonate in order to produce foam with immobilized diphosphonic acid ligands. The functionalized foam was able to complex 97.6% Eu(III) from a 0.0001 M solution in a background of 1-M nitric acid at a 30-min contact time, indicating that the ligands were present and accessible.

A second synthesis showed that functionalization was the same both at

the outer and inner portions of the foam, indicating no problem with accessibility of the reactants. That phosphorus capacity was, however, low. Experiments are in progress that are aimed at understanding the reason for the low capacity and how it might be increased.

We made a presentation of this work, entitled "Open-Celled Polymer Foams for Chemical Separations," at the Scientific Technical Exchange Meeting, University of Florida, March 25, 1997.

We submitted to the *Journal of Polymer Science* the following article:

S. D. Alexandratos, R. Beauvais, J. R. Duke, and B. S. Jorgensen,
"Functionalized Polymer Foams as Metal-Ion Chelating Agents with Rapid Complexation Kinetics."

Core Technology:
Materials Science—Thermodynamics

Principal Investigator: Mark A. Williamson

Task Description. The objective of this research is to study the vaporization chemistry, thermodynamics, and phase behavior of plutonium and americium oxychloride. These species are relevant to salt distillation performance. The oxychlorides could be present in the salt matrices that are to be treated by the distillation process, if complete oxidation of the plutonium and americium chloride does not occur. The data collected in this study could be used to better understand and model the distillation process.

Status/Accomplishments. Research at Los Alamos National Laboratory for the second quarter of fiscal year 1997 consisted of data analysis for plutonium oxychloride (PuOCl) vaporization studies and repair of the quadrupole mass spectrometer (QMS) system.

Vaporization data from the plutonium oxychloride (PuOCl) studies were analyzed. Briefly, PuOCl vaporizes by both congruent and incongruent processes. The incongruent process results in the formation of PuO_{2-x} when x is determined by the ratio of PuCl_3 (g) and PuCl (g). The degree of nonstoichiometry of PuO_{2-x} can also be deduced from x-ray diffraction data. X-ray data for the PuO_{2-x} residue obtained from the last vaporization experiment yielded a lattice constant

of 5.4052(6) Å. The composition of PuO_{2-x} with that lattice constant is $\text{PuO}_{1.975}$. Thermodynamic data for the system are currently being analyzed. A presentation of the work will be given at the High-Temperature Materials Chemistry Conference, May 18-23, 1997, at Pennsylvania State University, State College, Pennsylvania. The paper will be published in the *Journal of the Electrochemical Society*.

The mass spectrometer system was prepared for a set of americium oxychloride (AmOCl) experiments. While we were testing the QMS system, the high-Q head was damaged. A replacement head was obtained, but the mass range for that head is 1400 atomic mass units (amu), not the desired 500 amu. Because of the problems with the high-Q head, plus the fact that the power supplies are quite old and rely on tubes, we decided to replace all the electronics with Extrel's, newer C50™ controller electronics. The work will be finished in late April 1997, and we will then continue our study of AmOCl .

We continued our technical interaction with the DOE-STD-3013-96 thermal modeling effort, particularly regarding thermal conductivity.

Core Technology:**Synthesis and Structural Characterization of Plutonium(IV) and Plutonium(VI) Phosphates**

Principal Investigators: Wolfgang H. Runde
D. Kirk Veirs

Task Description. Phosphate coordination plays a significant role in actinide chemistry and potential stabilization processes, such as nitric acid/phosphoric acid treatment of combustibles. Despite the importance of actinide phosphate compounds, surprisingly little is known about their structure, bonding, stability, and spectroscopic properties. The objective of Los Alamos National Laboratory researchers is to develop a fundamental understanding of plutonium phosphate chemistry for synthesis of plutonium phosphate compounds, characterization of the solid state, and chemical behavior under radiolysis and aqueous conditions. Well-characterized plutonium phosphate compounds produced in this work will support plutonium solubility studies described elsewhere in this report.

Status/Accomplishments. As a prelude to work with plutonium, we prepared thermodynamically stable compounds in $\text{UO}_2(\text{NO}_3) \cdot x\text{H}_2\text{O}$ – H_3PO_4 – H_2O using precipitation from and hydrothermal treatment of aqueous solutions. Our data support the existence of three hydrated

compounds in the systems $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$, $\text{UO}_2\text{HPO}_4 \cdot x\text{H}_2\text{O}$, and $\text{UO}_2(\text{H}_2\text{PO}_4)_2 \cdot (\text{H}_2\text{O})2\text{H}_2\text{O}$. (See Fig. 11.) Our data also suggest that the total phosphate concentration in the mother liquors from which these solids precipitate may play a more critical role than the acidity of the liquors. The compounds are accessible through a number of synthesis routes. Herein we report reliable routes which yield reproducible results.

We prepared $\text{UO}_2\text{HPO}_4 \cdot x\text{H}_2\text{O}$ by mixing heated (65°C) solutions of $\text{UO}_2(\text{NO}_3) \cdot x\text{H}_2\text{O}$ and 75% phosphoric acid (H_3PO_4) in a $\text{U(VI)}:\text{PO}_4^{3-}$ of 1:2. The resulting precipitate, an amorphous mixture of two or more solids, was heated to 100°C and slowly cooled to room temperature. The precipitate slowly converted to lemon yellow single crystals over a period of 2 months; the crystals were removed from their mother liquor (pH 2). Data from single-crystal x-ray diffraction (XRD), powder x-ray diffraction (XRPD), and extended x-ray absorbance fine-structure (EXAFS) analyses allowed us to identify the solid as $\text{UO}_2\text{HPO}_4 \cdot x\text{H}_2\text{O}$.

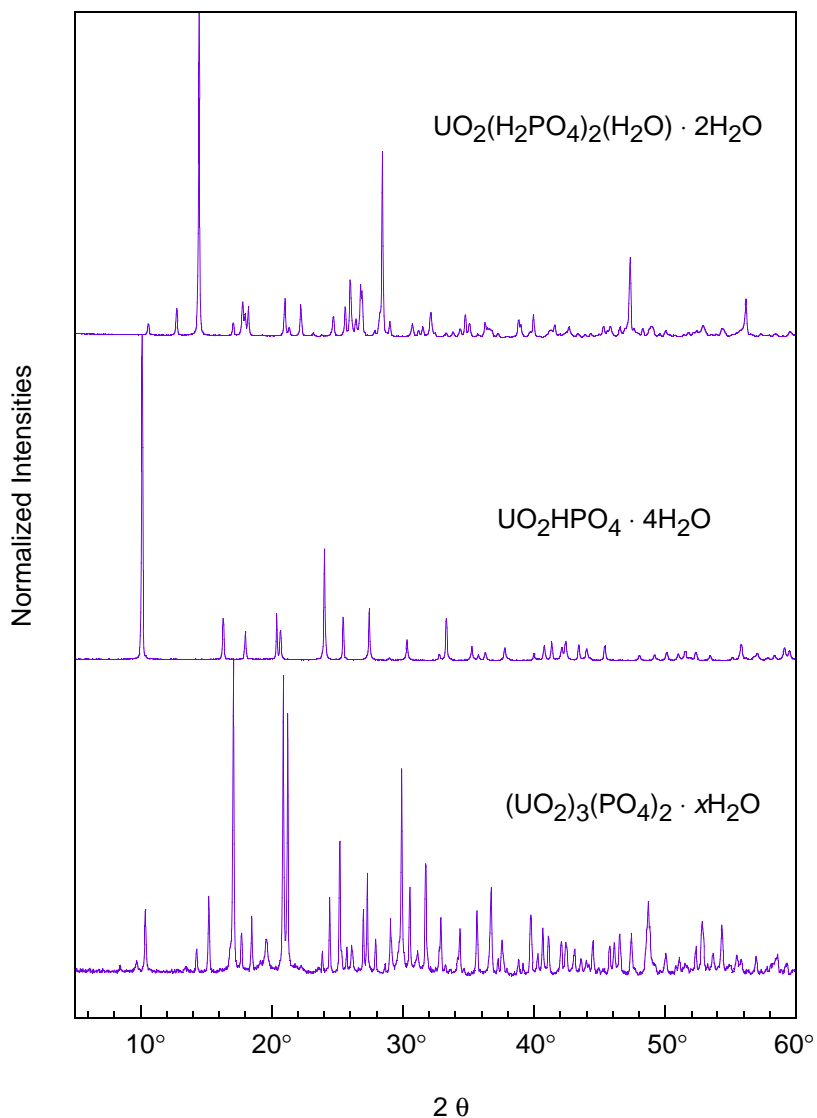


Fig. 11. Powder x-ray diffraction patterns of stable compounds in the $\text{UO}_2(\text{NO}_3) \cdot x\text{H}_2\text{O} - \text{H}_3\text{PO}_4 - \text{H}_2\text{O}$ system.

We prepared $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$ by repeatedly digesting $\text{UO}_2\text{HPO}_4 \cdot x\text{H}_2\text{O}$ in distilled water at 100°C . The pale yellow precipitate was removed from the mother liquor (pH 2) and characterized by XRPD. The peak positions and intensities of the resulting pattern are in general agreement with those reported for $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$ in the International Committee for Diffraction Data/Joint

Committee for Powder Diffraction Standards database.

We crystallized a large hexagonal plate-like crystal ($\sim 1\text{ cm} \times \sim 1\text{ cm} \times \sim 0.1\text{ cm}$) of $\text{UO}_2(\text{H}_2\text{PO}_4)_2(\text{H}_2\text{O}) \cdot 2\text{H}_2\text{O}$ from a saturated solution of $\text{UO}_2(\text{NO}_3) \cdot x\text{H}_2\text{O}$ and 75% H_3PO_4 . The crystal was removed from the mother liquor (pH < 1), characterized by both XRD and

XRPD, and identified as $\text{UO}_2(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$. An analysis of the mother liquor by ultraviolet-visible spectroscopy and comparisons with

a calibration plot revealed a $[\text{U(VI)}]$ in excess of 0.05 M and indicated the presence of soluble U(VI) phosphate complexes.

Core Technology:
Plutonium Phosphate Solution Chemistry

Principal Investigator: David G. Karraker (Savannah River Site)

Task Description. An attractive process for the destruction of combustible residues involves oxidation of organic material by nitric acid or hydrogen peroxide in a concentrated phosphoric acid (H_3PO_4) solution. After organic matter is oxidized, plutonium and other metal ions will accumulate in the phosphoric acid. This study of the chemistry of plutonium in concentrated phosphoric acid is aimed at determining the properties of plutonium in strong phosphoric acid and investigating methods for recovering plutonium and recycling H_3PO_4 .

Status/Accomplishments. The adsorption of plutonium from H_3PO_4 solutions was investigated by batch distribution studies over the range of 0.5–2 M H_3PO_4 . The results (Fig. 12) show a strong adsorption of Pu(IV) at low acidity and rapidly decreasing adsorption with increasing acidity. Pu(III) adsorption was found to be an order of magnitude less than that of Pu(IV). It is proposed that the adsorbing species is $\text{Pu}(\text{HPO}_4)_3$. Bio-Rad Laboratories analytical-grade anion resin (equivalent to Dowex® 1, 8% cross-linked, >200-mesh) was converted to phosphate form by washing with 2-M H_3PO_4 until a chloride test was negative. A weighed sample of resin was equilibrated with

H_3PO_4 solutions of Pu(IV); and for second determination, the Pu(IV) solution was reduced to Pu(III) by adding $\text{Fe}(\text{NH}_2\text{SO}_3)_2$. After 24 h equilibration, the solutions were sampled and the plutonium concentration was determined by liquid scintillation counting. The dry weight of the resin was determined by heating a weighed sample at 110°C for 2–6 h. K_d values were calculated from the $K_d = (C_0 - C) / C \times \text{wt of solution/resin dry wt}$, where C_0 is the initial plutonium concentration (disintegrations per milliliter-minute or d/mL-min) and C is the plutonium concentration after equilibration.

Measurements are still incomplete, but studies^{1,2} on the solubility of $\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}$ indicate that in this acidity range, species with Pu/ HPO_4 ratios of 1:2, 1:3, and 1:4 are the major complex species. The 1:2 complex is electrically neutral and thus would not adsorb; the 1:3 and 1:4 complexes may be negatively charged, and thus could ion-exchange. However, the decrease in K_d as the acidity increases suggests that the 1:3 complex is the adsorbing species; either the 1:4 complex is singly charged [$\text{Pu}(\text{HPO}_4)_4\text{H}_3^+$] or neutral. Another possibility is that mass action (competition from the H_2PO_4^- ion) accounts for decreased adsorption with increasing acidity.

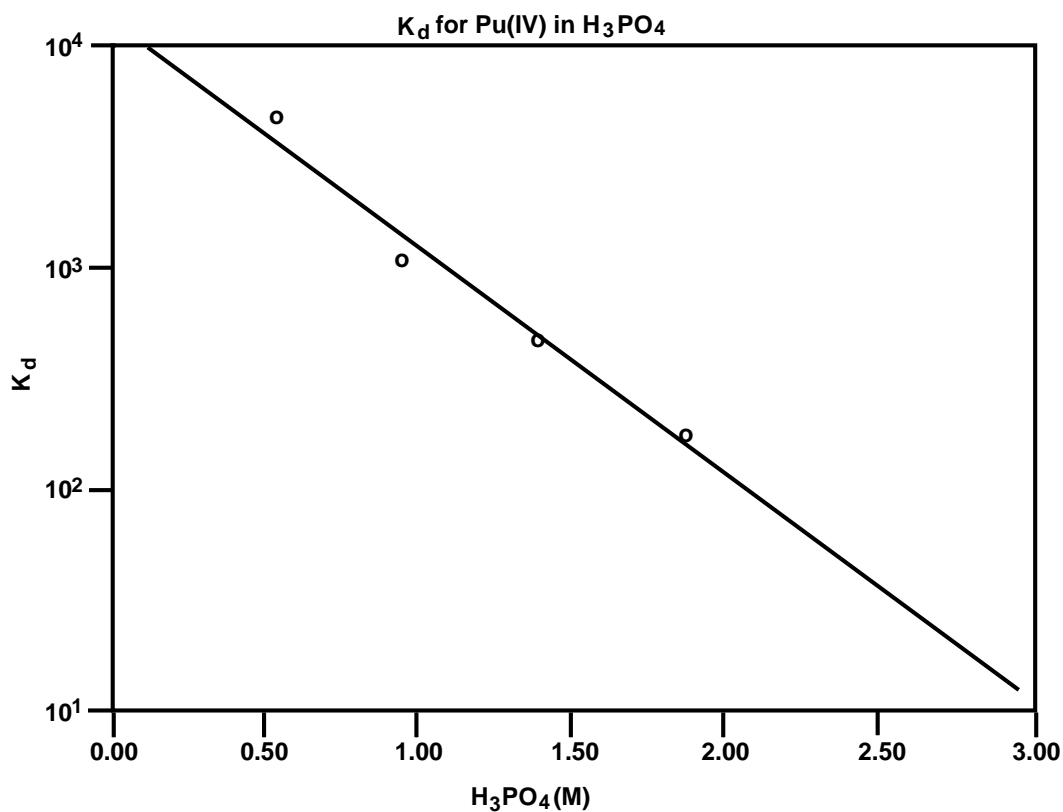


Fig. 12. Anion resin, H_3PO_4 form.

References:

1. E. L. King, "The Transuranium Elements," in *National Nuclear Energy Series, Division IV*, Vol. 14B, J. J. Katz and G. T. Seaborg, Eds., Part I, 638 (McGraw-Hill, Inc., 1949).
2. R. G. Denotkina, A. I. Moskvina, and V. B. Shevchenko, *Russ. J. Inorg. Chem.*, **5**, 731 (1960).

Core Technology:
Molten Salt/Nonaqueous Electrochemistry

Principal Investigator: Wayne H. Smith

Task Description. The purpose of this study is to develop a better understanding of the chemical behavior of actinide elements in molten salt systems. The experiments are to be carried out in a room-temperature molten-salt system (RTMS) in order to alleviate some of the technical difficulties associated with making accurate measurements in high-temperature systems. This study will include electrochemical and spectroscopic characterization of the actinides in this media. On the basis of the Core Technology reviews during the quarter, this project will be rescoped to address issues more directly germane to the Defense Nuclear Facilities Safety Board (DNFSB) 94-1 R&D project.

Status/Accomplishments. Thus far Los Alamos National Laboratory researchers have established an RTMS capability in the alpha wing located at the Los Alamos Radiochemistry Site. In preliminary experiments, we have duplicated published results for uranium. There are still some loose ends regarding uranium characterization that are currently being addressed before moving on to other actinide elements. A postdoctoral fellow has been recruited and hired. He is scheduled to arrive in April 1997 and will work full time on this project. An abstract has been submitted for a presentation on RTMS results to be given at the Plutonium Futures—The Science conference in Santa Fe, New Mexico, in August 1997.

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